NTNU – Trondheim
Norwegian University of
Science and Technology

Photocatalytic H2-production through photo-reforming of hydrocarbons

Synthesis and Photocatalytic appliacation of TiO2 Nanotubes

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Master's Thesis
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PREFACE

This study was carried out as a part of a master thesis at the Department of Chemical Engineering at the Norwegian University of Science and Technology.

During this work Magnus Rønning was the acting supervisor, and Charitha Udani the cosupervisor.

The field of research was selected due to a great interest in photocatalytical processes and the applications of them; as well as the effect that nanostructures could have in the catalyst for this kind of reactions.

The experiments that were carried differ from other previous work in the field in the attempt to study the effects on the reaction of introducing a nanotubular structure for the TiO2 as the catalyst precursor. The procedure used for the nanotube synthesis and preparation was developed during the experiments and differs from any previous research.

The goal was to test the Nanotube synthesis method efficiency, and see the effects that this kind of structure could have in alcohol photoreforming. At the same time one of the aims was to optimize the total catalyst mass in the reactor parameter while other parameters remained constant.

I would like to give thanks to my supervisor and co-supervisor for being patient and helping me, as well as those who helped me along, and gave me the necessary training:

Karin Wiggen for BET and TGA. Malin Sletnes for XRD, and Cornelis Gerardus for the Calcination.

Declaration of compliance

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

Place and date: Signature:

ABSTRACT

The main purpose of this Project is the study of the photocatalytical process of reforming alcohols in order to produce Hydrogen, using TiO_2 nanotubes as a precursor of the catalyst, and Copper as the electron transfer metal that coats the support.

The TiO_2 nanotubes were prepared using the hydrothermal synthesis method, which consist in nanotube formation parting from P-25 TiO2 powder in a NaOH 10M solution stirred and set at 110ºC. After that the product followed a washing process via centrifugation, being the main purpose of that procedure the neutralization of the ph and the proper formation of the nanotube structure in our catalyst. Before centrifugation, other alternative processes were tried without success.

The BET analysis done on the precursor revealed that the surface area was higher than the P-25 used in the synthesis but still relatively low compared to the values found in literature. This was mainly attributed to the washing process nature, and the poor control over the temperature during the hydrothermal synthesis.

The Catalyst was prepared using the Incipient Wetness Impregnation method coating the precursor with Copper. The Copper loading was 5% weight of the catalyst.

The reactions were performed in a photoreactor, and the wavelength selected for the UV irradiation of the reaction mix was UVC, and the alcohol selected to be reformed was Methanol.

Since the concentration of MeOH in the reactor was fixed at 50%vol, the only parameter that was changed was the total mass of the catalyst in the reactor. The experiences that were made involved catalyst mass of 100, 150, 200, 250 and 300 mg.

The experiments with 150, 200 and 250 mg of catalyst load, led to a very small hydrogen production after 8 hours of reaction time. The hydrogen flow produced was detected by the Chromatographer but couldn’t be quantified.

For the reactions with 100 and 300 mg of catalyst mass, no hydrogen production was detected in 22 hours of reaction time. This experience could be used to establish the borders of the efficient quantity of catalyst powder in the reactor for the hydrogen production.

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INTRODUCTION

The Project focuses on the study of the photocatalytic reaction of Alcohols in order to produce Hydrogen. This field of investigation is considered as one of various attempts to consolidate new ways of implementing renewable energies and pollutant-free processes. The process that is researched focuses on a H_2 production via, that uses light radiation as a source to activate the catalyst of the reaction. The process is considered to not produce big quantity of emissions, and relies on a renewable source of energy to activate the catalyst.

In addition, it must be noticed that the source of Hydrogen for the reaction that takes place in the process consist on different alcohols that are a common waste product of different chemical processes. So, even though the technology depicted is still young and needs further research and development, the applications of it as a secondary process for a plant that produces those alcohols as a by-product are clearly visible.

In this project the main innovation is that the catalyst was prepared in form of TiO_2 nanotubes in order to study the effects of this display on the Hydrogen production and the different parameters of the reaction.

The synthesis of the nanotubes and preparation of the catalyst and testing the effect in the photochemical reaction are the main aims of the project, and different methods were tried and failed in order to obtain the catalyst used in the reaction.

STATE OF THE ART

The technology investigated in the project has been researched in previous articles and publications. There are a few principal variables that change between the previous researches on the subject:

-The use of different metal combinations for the synthesis of the catalyst and the mass of it, as well as different loadings of the support material in the catalyst.

-Different alcohols and hydrocarbons have been proposed as the reactant that is to be reformed.

-the wave length of the light radiation used to activate the catalyst (UV spectrum).

-the particle size of the catalyst.

There are already some applications of photocatalytic processes involving TiO_2 and its special properties as a semiconductor that are currently in use in industry.

There are as well a great number of publications referring to other different photocatalytic reactions that differ from the reforming of hydrocarbons in order to obtain Hydrogen.

The use of the TiO_2 properties as a photo-catalyst precursor has seen success in some of its applications in the industry as well as publications. As a semiconductor and its ability to form radicals in red-ox reactions after the activation by UV light means a great potential in the catalysis of numerous reactions.

1. THEORETICAL BASES

Photochemical Reactions

In order to understand the process studied in the project, some principles must be understood.

Photocatalysis is one of the many fields in photochemistry, which is defined as a discipline inside chemistry that studies the reactions in which the absorption of light is involved. The Grotthuss–Draper law states that for a photochemical reaction to take place, light must be absorbed by a chemical substance; and for every photon of light absorbed, only one molecule can be activated for the reaction to take place.

The photochemical reactions take place when the light absorbed provides the activation energy for the molecule, or changes the symmetry of the electronic configuration allowing other paths of reaction.

The efficiency with which a given photochemical process occurs is given by its Quantum Yield (Φ). Since many photochemical reactions are complex, and may compete with unproductive energy loss, the quantum yield is usually specified.

The Quantum Yield is defined as the number of moles of a stated product produced, per einstein of monochromatic light absorbed. An Einstein is defined as a mole of photons.

[N. J. Turro, V. Ramamurthy, J. C. Scaiano Modern Molecular Photochemistry of Organic Molecules. University Science Books, Sausalito, 2010]

Photocatalysis

Photocatalysis is known as the acceleration of a photoreaction in presence of a catalyst. The catalyst of the reaction is activated by light instead of thermal energy, and accelerates the reaction without been consumed.

Two main types of photocatalysis are distinguished: homogeneous photocatalysis and heterogeneous photocatalysis.

In homogeneous photocatalysis, the reactants and the catalyst are in the same phase. An example of this process is the hydroxyl radical production by ozone in Photo-Fenton systems (hydrogen peroxide and Fe cation). This kind of reactions is usually faster than the other kind.

In heterogeneous photocatalysis reactant and catalyst are in different phases. The catalyst in this kind of reactions is usually a transition metal oxide and semiconductor. Semiconductors have a void energy region in which there are no energy levels to promote the recombination of an electron and hole that is produced when the solid is activated by light. That void region extends from the top of the filled valence band to the bottom of the vacant conduction band and is called the band gap. In order for a photon to be absorbed, it must have greater energy than the band gap of the material. Then an electron is excited and moves from the valence band to the conduction band creating a hole with positive charge in the valence band. The excited electron can react with an oxidant and the positive holes can react with a reductant, so for the reaction to take place, red-ox reactions take place at the semiconductor.

(Linsebigler, Amy L.; Lu, Guangquan.; Yates, John T. (1995))

[Pier Luigi Gentili, Fausto Ortica, Fausto Elisei, Margherita Giuliobello. Band Gap engineering of Photo-Catalyst for Water Splitting (2006)]

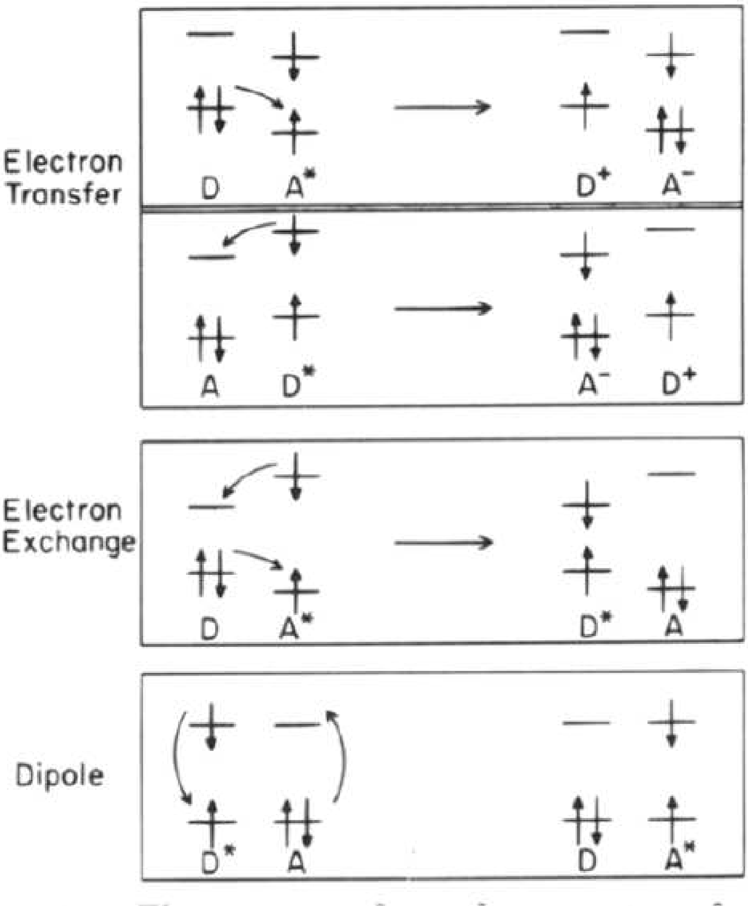
Reaction Mechanism

There are two main reactions mechanism for the reaction to take place, once the catalyst has absorbed light. The deexcitation process can occur by electron transfer or energy transfer.

The electron transfer process consists in an electron movement from the occupied orbital of a donor to a free orbital of an acceptor. The reaction can start either in the donor (D-D*) freeing the electron, or in the acceptor (A-A*) taking it; but it is needed that the orbitals of the donor and acceptor overlap. After the transfer both donor and acceptor become ions (D+ and A-)

An energy transfer process can take place by electron exchange or dipole-dipole coupling. Electron exchange occurs by two independent electron transfer steps that take part simultaneously. As electron transfer process, it requires orbital overlap between donor and acceptor.

Dipole-dipole coupling occurs by a Coulombic resonance interaction. This process does not require the orbital overlap between of the donor and acceptor.



Schematic figure of the deexcitation process after photoactivation of the catalyst

(Amy L. Linsebigler, Guangquan Lu, and John T. Yates, Jr. (1994))

Alcohol reforming

The reaction that takes place in our process is a photo-catalysed reformation of a simple alcohol.

There are a few possible reactions that can take place at the reactor in presence of the activated catalyst.

At the valence band the oxidation of water in order to obtain hydroxyl radical is possible.

$$-OH + h^+ \rightarrow \cdot OH$$

This radical is highly reactive and of great importance for the reforming reaction of the alcohol.

At the conduction band the reaction that can take place is the reduction of oxygen molecule obtaining superoxide.

$$O_2 + e^- \rightarrow \cdot O_2^-$$

Apart from the former reactions, these are possible.

Oxygen formation via water oxidation:

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$

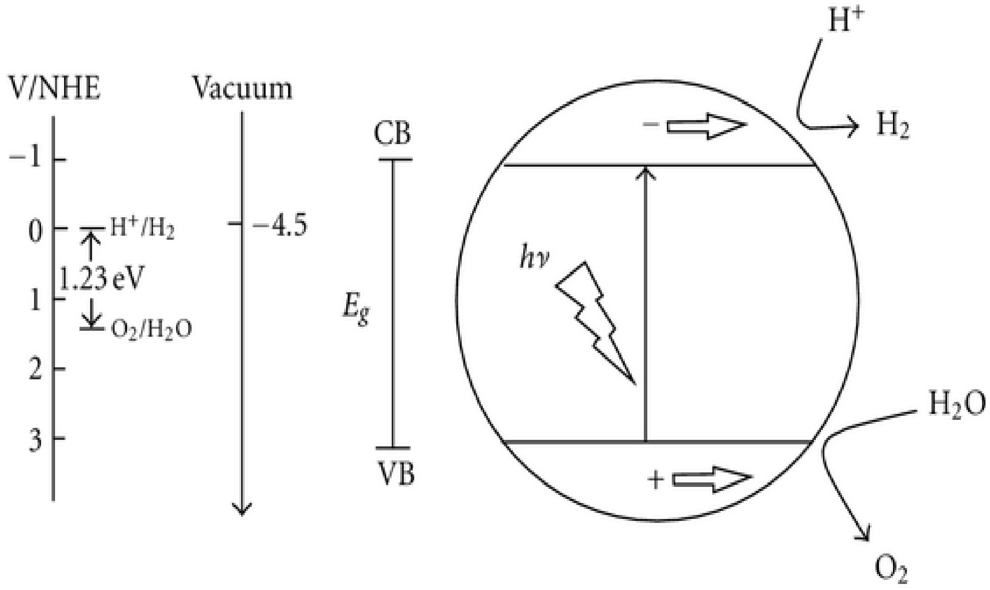
This oxygen is consumed in the superoxide formation, or can contribute in water synthesis.

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O$$

As it was stated, both superoxide and hydroxide are radicals and therefore they are very reactive and play a major role.

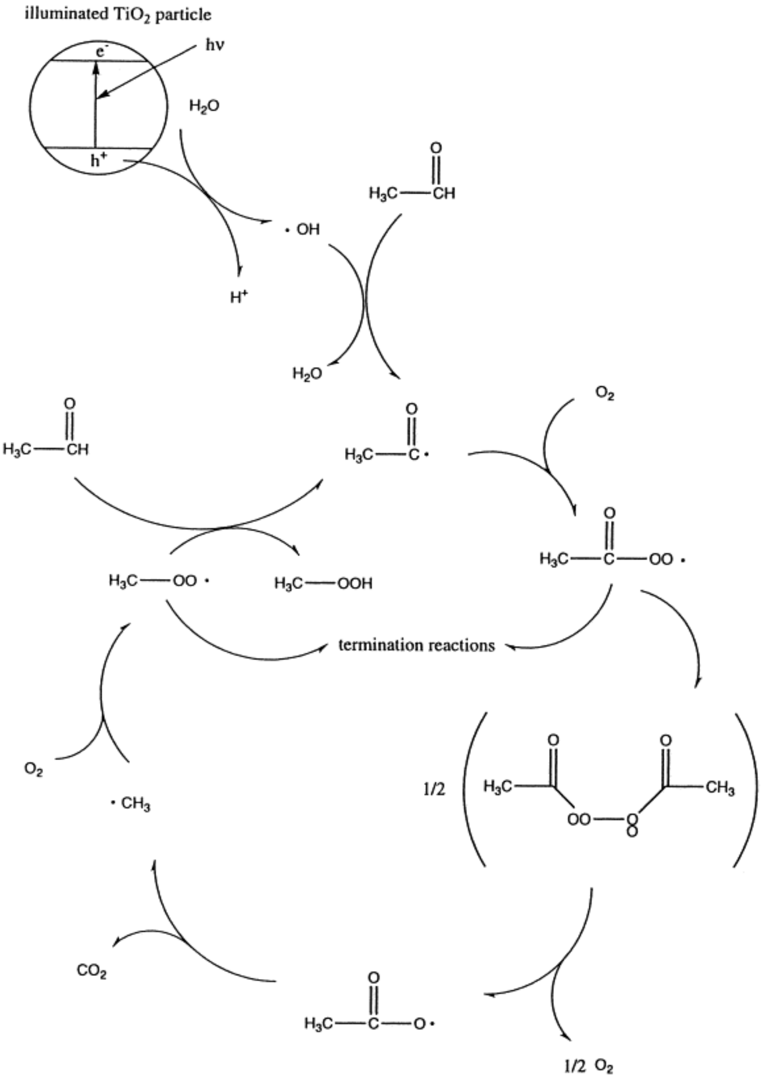
A possible mechanism for the photoreforming of alcohols on TiO2 involves the oxidation of water molecules producing hydroxyl radicals, which abstract an alpha hydrogen to create a •RCH2–OH radical. The radical is further oxidised to an aldehyde.

If we consider the simplest alcohol as the substrate (methanol), at first water splitting occurs on the surface of TiO2, but its rate is limited by accumulation of holes and hydroxyl radicals. In the second step, the photogenerated holes oxidise methanol to formaldehyde, then further oxidized by both hydroxyl radicals and holes to produce formic acid. In the third step, formic acid is decarboxylated to release CO2. H^+ ions are created in different steps, and they transfer to CuO and are oxidized to hydrogen by the photogenerated electrons.



Basic mechanism of photocatalytic water splitting

[Ilenia Rossetti, “Hydrogen Production by Photoreforming of Renewable Substrates,”2012]



photocatalytic oxidation of acetaldehyde.

[Akira Fujishima, Tata N. Rao, Donald A. Tryk, Titanium dioxide photocatalysis, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, Volume 1, Issue 1, 29 June 2000]

Titanium Dioxide as catalyst

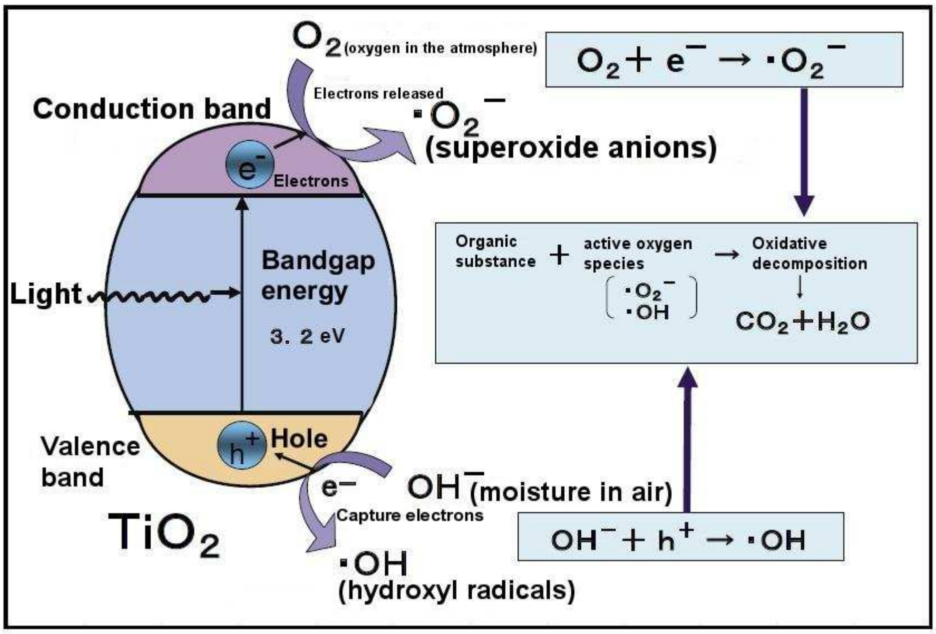
Titanium Dioxide (TiO2) is one of the most used semiconductors in photo-activated catalysts.

This is due to its ability to absorb UV light, and the effect it has on the electronic structure of the particle.

As a semiconductor it has a Valence band that tends to create a hole of positive charge, by the migration of an electron to the Conduction band. This migration gives the particle oxidising power in the Valence band, and reductive power at the Conduction band.

Titanium dioxide exists in nature as minerals rutile, anatase and brookite. The first two have a tetragonal crystal system and brookite has an orthorhombic.

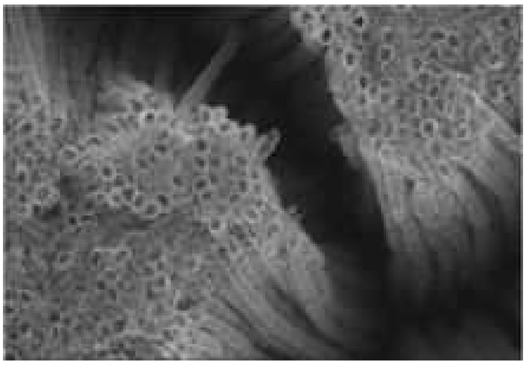
The TiO_2 utilized in the experiences of this project is a commercial form known as P25. That variety is known for a specific particle size (average 21nm) and surface area.



Scheme of the TiO_2 particle and its activity in radical formation

TiO_2 Nanotubes

Anatase and rutile can be converted by hydrothermal synthesis to delaminated inorganic nanotubes. The tubes have an outer diameter of 10 to 20 nm and an inner diameter of 5 to 8 nm and have a length of 1 µm. There's an alternative path for the synthesis known as electrochemical oxidation route but in the project the hydrothermal synthesis was used.



Titanium oxide nanotubes, SEM image.

This synthesis method basically consists in diluting the Titanium dioxide powder in a NaOH 10M solution, and stirred it for a period of time of at least 20 hours at a constant temperature of 110ºC, which corresponds to the boiling temperature of the alkaline solution.

Similar to common TiO2 powder, the titanium oxide nanotubes are also white colour powder. The optical bandgap energy calculated from the ultraviolet–visible light absorption spectra by assuming indirect transition of TiO2 is approximately 3.41 ~ 3.45eV, which value is slightly larger than that of anatase (3.2 eV) and rutile (3.0 eV) crystals.

[Tohru Sekino, Synthesis and Applications of Titanium Oxide Nanotubes]

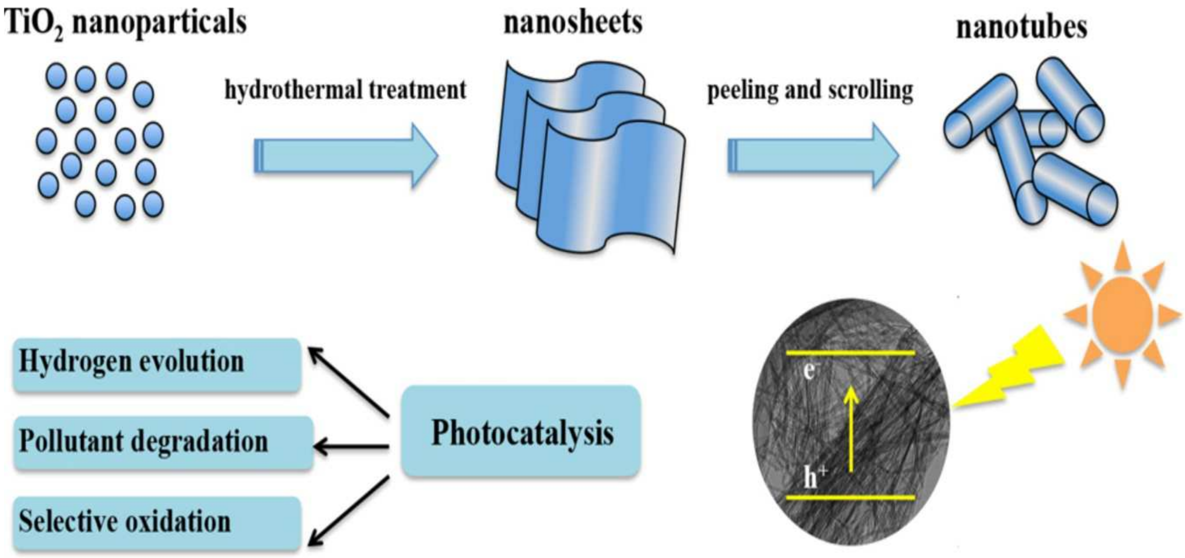
The geometry of the nanotubes can be defined as long, hollow cylinders. The large specific surface area of TNTs (range from 100 to 478 m2/g) and pore volume (from 0.25 to 1.1 cm3/g) provide more effective reaction sites for photocatalysis.

After having obtained the TNTs from the hydrothermal synthesis the washing process is an important step for the production of nanotubular structures.

Before the washing process lamellar sheets are formed during the hydrothermal process; but the washing process removes the electrostatic repulsion and results in the formation of the nanotube structure.

The nanotubes formed by the hydrothermal method have ion-exchange ability, and this offers an opportunity for further modification of TNTs like doping with other ions to improve the activity.

The interest in TNTs as a photocatalyst is growing for the photo excited oxidation/reduction reactions that mainly include hydrogen production from water splitting, purification of groundwater and wastewater, as well as selective oxidation of organics.



Schematic process of nanotube synthesis

[Nan Liu, Xiaoyin Chen, Jinli Zhang, Johannes W. Schwank, A review on TiO2-based nanotubes synthesized via hydrothermal method: Formation mechanism, structure modification, and photocatalytic applications, Catalysis Today, Volume 225, 15 April 2014]

Applications

There are some different applications of the technology involve in photocatalysis, and most of them are related to “clean” energy sources and alternatives to obtain different compounds.

Some of the Applications are now formal processes that are run in the industry, but others are still in a development stage and still being researched.

Photocatalytic water splitting

Is a photocatalytic reaction in a photoelectrochemical cell used for the dissociation of water into its constituent parts, hydrogen (H_2) and oxygen (O_2), using either artificial or natural light. It’s commonly referred as “artificial photosynthesis”.

It’s becoming more and more important as a source of hydrogen as a fuel (an alternative to other non-renewable fuels as oil that are becoming expensive and scarce) in a clean process that uses a renewable resource.

Photocatalytic water splitting has the simplicity of using a powder in solution and sunlight to produce H_2 and O_2 from water and can provide a clean, renewable energy, without producing greenhouse gases or having many adverse effects on the atmosphere.

Photocatalysed Disinfection of water

TiO_2 catalyst is used in this process due to the radical reactions that take place in the surface of the catalyst, and the natural disinfectant effect of UV radiation on water.

The main advantages of this process are the stability of the materials involved and the absence of an energy input requirement, which make this process a very interesting solution in developing countries.

Conversion of carbon dioxide into gaseous hydrocarbons

This process uses TiO_2 nanoparticles in presence of water producing hydroxide radicals and protons. The reactions lead to the formation of methane from CO_2.

It has been shown that the incorporation of carbon based nanostructures such as carbon nanotubes and metallic nanoparticles enhance the efficiency of these photocatalysts in the reaction.

Decomposition of crude oil with TiO2 nanoparticles

Using titanium dioxide photocatalysts and UV-A radiation, the hydrocarbons found in crude oil can be turned into H_2O and CO_2. These particles can be placed on floating substrates, making it easier to recover and catalyze the reaction.

Air purification

The use of the catalyst particles and a UV lamp in an air filter has been commercialised in the latest years. The Air that crosses the filter gets rid of some contaminants that are oxidized into familiar compounds like H_2O and CO_2.

Decomposition of poly-aromatic hydrocarbons

Poly-aromatic hydrocarbons present in crude oil, are solved and extracted with Triethylamine. After their removal they are treated with TiO_2 slurries and UV light and degraded via photocatalytic reaction. This process has contaminants recoveries of 93-99% and constitutes an environmental friendly process.

ANALYSIS TECHNIQUES

BET

The BET analysis technique was used to check the surface area of our catalyst precursor. This technique is based on the BET theory which has its name as an acronym of Brunauer–Emmett–Teller, its developers.

That theory tries to explain the adsorption of gas molecules on a solid surface and specifically refers to multi-layer adsorption of non corrosive gases.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, with the following hypotheses:

(a) Gas molecules physically adsorb on a solid in layers infinitely

(b) There is no interaction between each adsorption layer

(c) The Langmuir theory can be applied individually to each layer.

The BET theory can be derived similar to the Langmuir theory, but by considering multilayered gas molecule adsorption, where it is not required for a layer to be completed before an upper layer formation starts.

The authors made 5 main assumptions:

- Adsorptions occur only on well-defined sites of the sample surface and one per molecule.

- The only molecular interaction considered is that a molecule can act as a single adsorption site for a molecule of the upper layer.

- The top molecule layer is in equilibrium with the gas phase

- The desorption is a kinetically-limited process, and a heat of adsorption must be provided

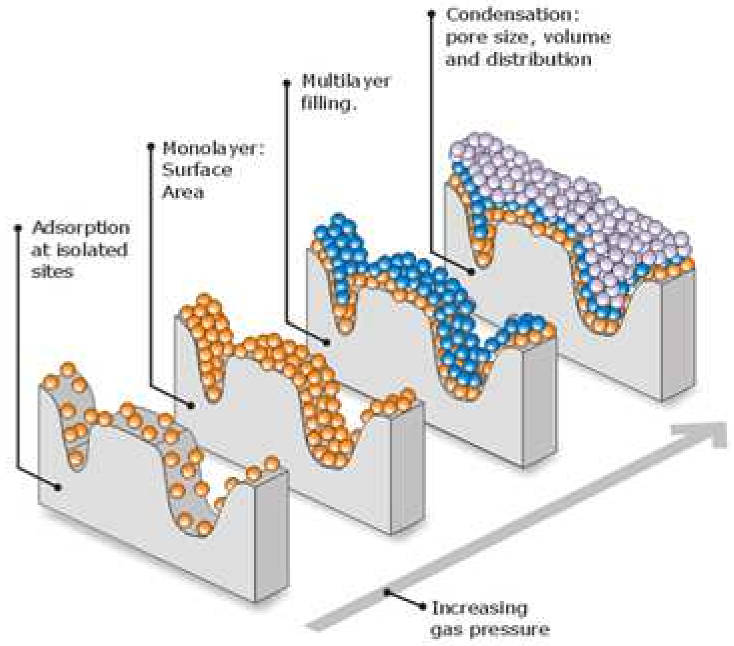
- At the saturation pressure, the molecule layer number tends to infinity.

BET theory has been applied to measure the specific surface area of activated carbon, or in the field of solid catalysis, where the surface area of catalysts is an important factor in catalytic activity.

Before the specific surface area of the sample can be determined, it is necessary to remove gases and vapours that may have become physically adsorbed onto the surface.

The outgassing conditions defined by the temperature, pressure and time should be chosen so that the original surface of the solid is reproduced as closely as possible. Outgassing of many substances is often achieved by applying a vacuum, by purging the sample in a flowing stream of a non-reactive dry gas.

Sometimes, elevated temperatures are used to increase the rate at which the contaminants leave the surface.



Multilayer gas adsorption, BET.

[Kenneth S.W Sing, Adsorption methods for the characterization of porous materials, Advances in Colloid and Interface Science, (1998)]

XRD

English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence.

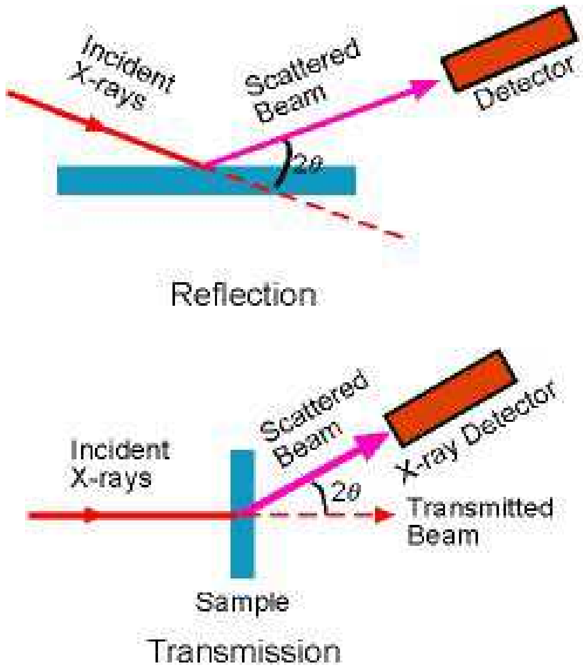
The XRD technique takes a sample of the material and places a powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the inter-atomic spacing.

The sample is placed in a very thin film at the sample holder and then it’s impacted by an incident x-ray beam that hits the sample and is diffracted by a determined angle.

That diffraction is caused by the atomic planes of the crystalline sample.

Powder XRD (X-ray Diffraction) is the most widely used x-ray diffraction technique for characterizing materials. The sample is usually in a powdery form, consisting of fine grains of the crystalline material. The crystalline domains are randomly oriented in the sample, so when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks. The positions and the intensities of the peaks are used for identifying the structure of the material.

Powder diffraction data can be collected using either transmission or reflection geometry, given the fact that the particles in the powder sample are randomly oriented.



Transmission and reflection data collecting in XRD

The main characteristics of this analysis technique are:

- It’s a non destructive technique, fast and the preparation of the sample is simple.

- It has a very high accuracy in calculating de atom spacing.

- The technique can be done *in situ*.

- Allows the analysis of single crystal, poly and amorphous materials.

- Different standards are available for a vast array of materials.

The technique identifies crystalline phases and orientation, and allows determining structural properties and atomic arrangements.

[X-ray Diffraction, by B.E. Warren, General Publishing Company, 1969, 1990 (Classic x-ray physics book)]

MICRO-GC

This analysis technique is a compact and simple form of the Gas Chromatography process, and allows detecting different components in a sample that can be vaporized without decomposition.

The technique is based in column that contains a stationary phase that usually consist on a microscopic layer of liquid or polymer on an inert solid support. There is another phase, which is called the mobile phase; which is a carrier inert gas such as helium or Argon or an unreactive gas such as nitrogen.

The gaseous compounds being analyzed are dragged by the mobile phase and interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound. The column through which the gas phase passes is located in an oven where the temperature of the gas can be controlled and the concentration of a compound in the gas phase is solely a function of the vapour pressure of the gas.

In the process a known volume of gaseous analyte is injected into the head of the column, usually using a microsyringe. The carrier gas sweeps the analyte molecules through the column and this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column.

The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. A detector is used to monitor the outlet stream from the column so the time at which each component reaches the outlet and the amount of that component can be determined.

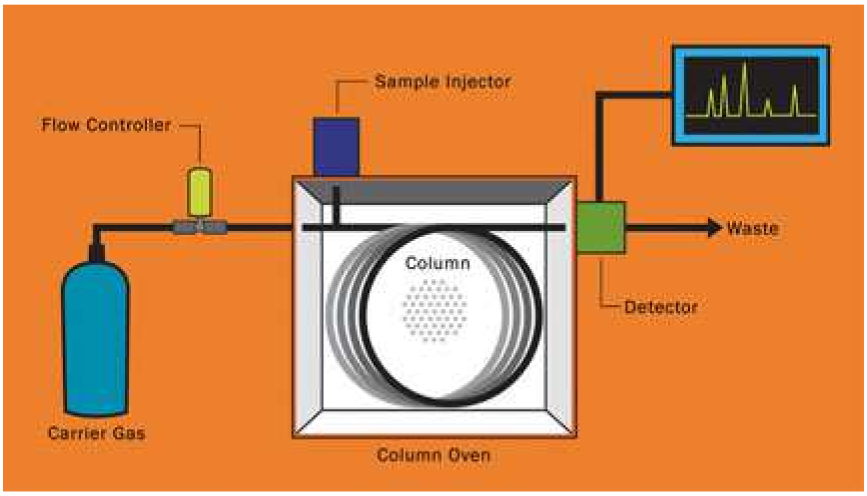
Generally chromatographic data is presented as a graph of detector response against retention time which is called a chromatogram. This provides a spectrum of peaks for a sample representing the analytes present.

The area under a peak is proportional to the amount of analyte present in the chromatogram. By calculating the area of the peak the concentration of an analyte in the original sample can be determined.

In most modern devices computer software is used to draw and integrate peaks.

The main particularities of Micro Gas Chromatography are that the equipment has small overall dimensions and portability compared to more traditional chromatographers, the run time is relatively short and has a low consumption of the carrier gas.

Typically, the Micro GC equipment uses from two to four chromatography columns in which the sample is analyzed.



Scheme of a Gas chromatography unit.

OPTIMIZATION

The reaction rate in this process is dependant of both the catalyst mass and the reactant concentration.

The reaction rate increases as a first order reaction, but it tends to a zero order as soon as it starts to be an excess of the catalyst mass or the reactant.

As the reactant concentration increases, the hydroxilic absorption sites in the catalyst get saturated. This is translated to reactant mass not been transformed. The optimal concentration of reactive would be just before the level of reaction changes.

When there is an excess of catalyst mass, the powder in the reactor blocks the irradiation of other catalyst particles in the reaction mix. This translates into a part of the total catalyst amount, not been activated by the UV light, and therefore not playing its role as a catalyst in the reaction.

2. EXPERIMETAL PROCEDURE

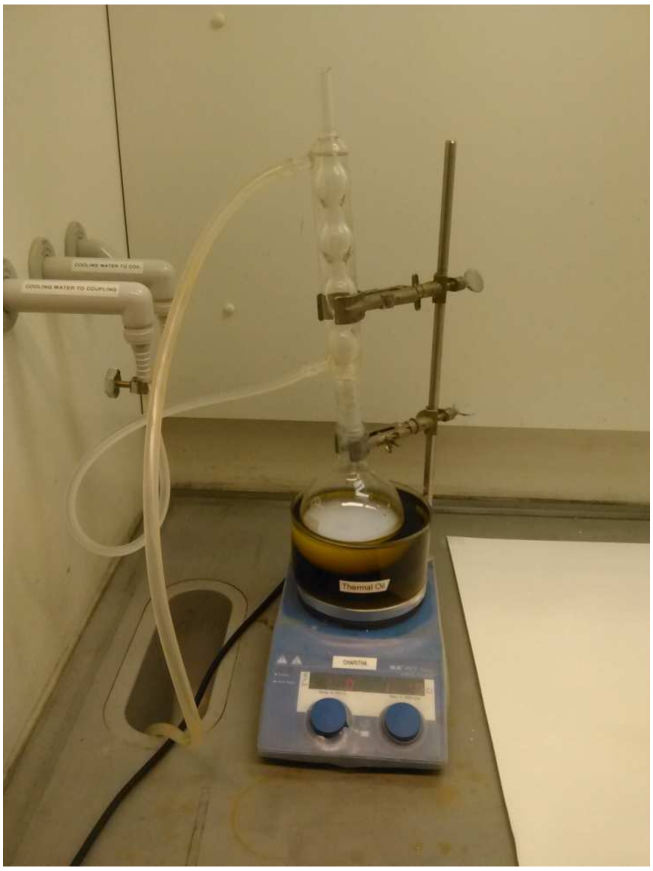
The experiments that were run can be divided in three different steps of the whole process: the preparation of the catalyst, the analysis of the catalyst and the reaction.

The experiments were held at the lab 317 in the third floor, and 217 in the second floor both in K5 building.

CATALYST PREPARATION

In order to produce the TiO_2 the hydrothermal synthesis method was used.

A NaOH 10M solution was prepared diluting 80g of NaOH pellets in 200ml of water. Then 220 mg of P25 TiO_2 were added to the solution and put in a matrass. The solution was set in a heated bath at 110ºC and stirred with a magnetic stirrer at 1000rpm. The set up for the synthesis included a cooling system to condensate the evaporated solution and lead it back to the matrass. This process of hydrothermal synthesis of the nanotubes was held for 48h before starting with the washing process.



Hydrothermal nanotube synthesis set up

After 48h at the heated bath, the solution was poured in a flask and distributed in six different plastic tubes for centrifugation. The tubes were weighted before being put in the centrifuge, and filled with the adequate amount of the distilled water so they weighted the same.

Then they were set in the centrifuge at 11000 rpm during 5 min so the solid catalyst separated from the liquid phase and sticked to the wall. The liquid phase was removed measuring its ph and the tubes were refilled with distilled water and set again in the centrifuge. The process was repeated until the ph of the liquid phase reached a value of 7 and the catalyst powder was neutralized.

Centrifuge during washing procedure.

After the centrifuging the solid phase was collected and moved to a ceramic recipient. That recipient was put in a high temperature furnace and was left at 110ºC during 4 hours in order to dry the powder. Then the powder was collected in a sample holder and stored.

High temperature furnace.

When the amount of powder processed like it was mentioned before was enough, the incipient wetness impregnation method was used to add the copper load to the powder. But a small quantity of TiO2 nanotubes powder was saved in order to run the BET analysis.

Incipient Wetness Impregnation

To add the copper loading the desirable amount of $CuN_2O_6{:}3H_2O$ was diluted with distilled water and added to the crushed TiO_2 nanotubes powder. Enough distilled water needed to be added in order to solve the copper precursor and to fill the pores of the TiO_2 nanotubes. Then it was carefully mixed and was set in the oven at 70ºC during one night to dry the powder.

The next step in the preparation of the catalyst was the calcinations of the powder. The catalyst was put in a ceramic recipient inside of the high temperature furnace. The furnace was programmed to increase the temperature 5º every minute until reaching the temperature of 300ºC. Then that temperature was held for 4 hours.

Catalyst powder after calcinations.

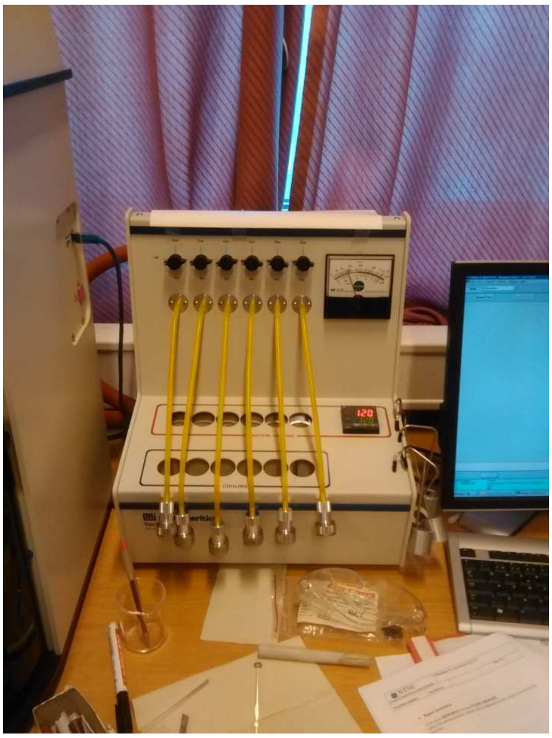
After that the powder was crushed and sieved with the purpose of having a particle size smaller than 53μm. The mass of powder that didn't pass through the holes of the sieve tray was crushed again until it was able to go through the holes.

At the beginning of the experiments, another process was tried for the washing of the powder. A vacuum filtration was the first choice, but it was discarded after a time due to the bad results that were being obtained. The details of the process are specified in the annexes.

CATALYST ANALYSIS

In order to analyse the surface area, the pore volume and the pore size of our catalyst precursor, a BET analysis was done.

A very small amount of TiO_2 nanotubes powder was separated from the rest and crushed, and it was collected in a BET sample tube. For the analysis it was needed to weight the sample tube and the sample tube plus the sample so the powder mass that was going to be analyzed could be inputted later in the program. Then the tube was put at the De-gas equipment at the heating station (120ºC) at vacuum pressure and was left overnight.



BET De-gassing unit.

After the De-gas, the sample was left to cool down and the container for the liquid nitrogen of the BET was filled until the level reached the correct spot in the level indicator. Then the container was attached to the lever of the BET analysis machine, and the sample tube was attached to the sample holder.

Using the computer with the adequate software, the experience was arranged. A file was created in which the sample mass had to be inputted, as well as the information that was wanted to appear at the report. Then, the sample port to which our sample tube was attached and the file with the information for the experience that was created in the last step had to be selected in order to start running the analysis.

BET analysis unit

Liquid Nitrogen container for BET

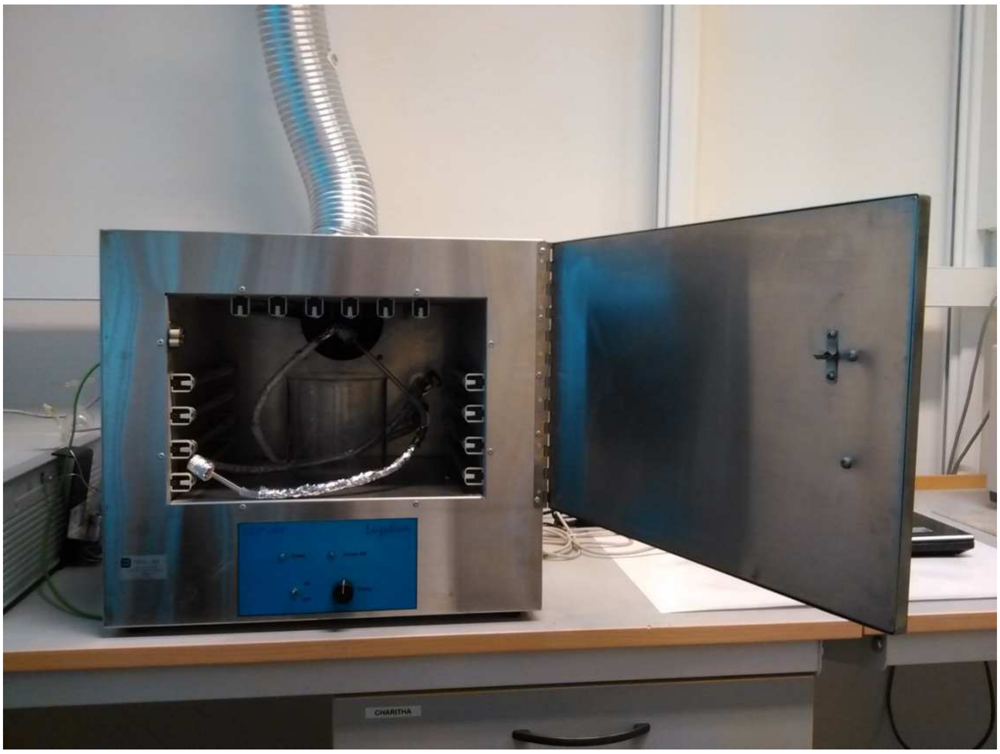
The process started with a leak test that lasted around 30 minutes and then the analysis began. After 5 hours the results were shown with the software.

Another analysis technique was used in a different sample. That sample was a Catalyst powder of TiO_2 with a gold loading, and the technique used was X-ray diffraction. Since the sample was not used in a reaction and was different from the catalyst synthesised for this report, the details of the analysis are covered in the annexes.

REACTION

SET UP

The reactor is placed in a metal container with a door to access the interior. Along the walls and the ceiling of the container there’s an array of UV lamps that can be configured for different wavelengths. Next to the container is a MicroGC unit that is used to measure and record the hydrogen output of the reactor.



Reactor Set up

In order to force the hydrogen produced in the reaction to flow through the pipe and reach the MicroGC, An Argon flow is used. It reaches the reactor through a pipeline and exits it dragging the hydrogen to the chromatographer. The pipe that goes from the reactor to the MicroGC has thermal insulation and is heated in order to make sure that there’s no liquid entering the column, as it could damage the instrument.

The MicroGC outlet is connected to the ventilation pipe, due to the fact that the sample is eliminated after the analysis. The chromatographer has an Argon inlet, as Argon is the carrier gas of the column.

MicroGC unit, and heated inlet of the gas sample.

Two computers are used to control and run the process. One of them is used to turn the stirrer of the reactor container on, and to manipulate the UV lamps.

The other computer controls the argon flow to the reactor and the MicroGC, and records the measurements of hydrogen flow produced in the reaction per cycle.

The reactor that is fitted in the container consists on a quartz recipient and a lid that has to holes on its surface (in order to attach the argon inlet and the gas outlet). The lid is attached to the recipient using a rubber band and a locking mechanism that ensures that the whole configuration is sealed.

Since the inlet and outlet lines to the reactor need to enter the reactor container and be flexible, they are made of rubber in that part. However, they are exposed to the UV radiation generated by the lamps and that could affect the material and deteriorate its properties; so they are cover in aluminium foil to prevent that effect. In the line that introduces Argon in the reactor there is a valve that can be regulated to allow different flows of Argon. That valve has to be calibrated using a bubble flow meter present in a secondary line, establishing a relation between the opening percentage, and the actual Argon flow in the line. That process is covered in the annexes.

REACTION PROCEDURE

The first step arranging the reaction was the preparation of the alcohol and water solution.

For the experiences one single alcohol was used (Methanol) and the concentration of the solution with water was fixed at 50% vol for all the reactions. The parameter that changed between the different experiences was the mass of the catalyst in the reactor.

In order to add the desirable amount of catalyst to the reactant solution, the reactor recipient with the solution needed to be continuously stirred (using a magnetic stirrer also present during the reaction), and the catalyst was slowly added in order to prevent it to stick to the walls.

After that, the lid and the locking mechanism were attached, the reactor was placed into the reactor set up and the Argon inlet an outlet lines were connected. Accessing the reactor set up software the stirrer was activated, but the lamps were not activated yet. Opening the valve for the argon flow to its maximum we allow the Argon flow to enter and bubble in the reactor for thirty minutes.

Reactor container during the Argon flow ventilation.

After the ventilation the Argon flow was set to 10ml/min which translates to a valve aperture of 6.5%. Then the UV lamps were connected and set at a wave length proper of UVC radiation, and the MicroGC was initiated using the software of the computer.

Reactor set up during reaction process

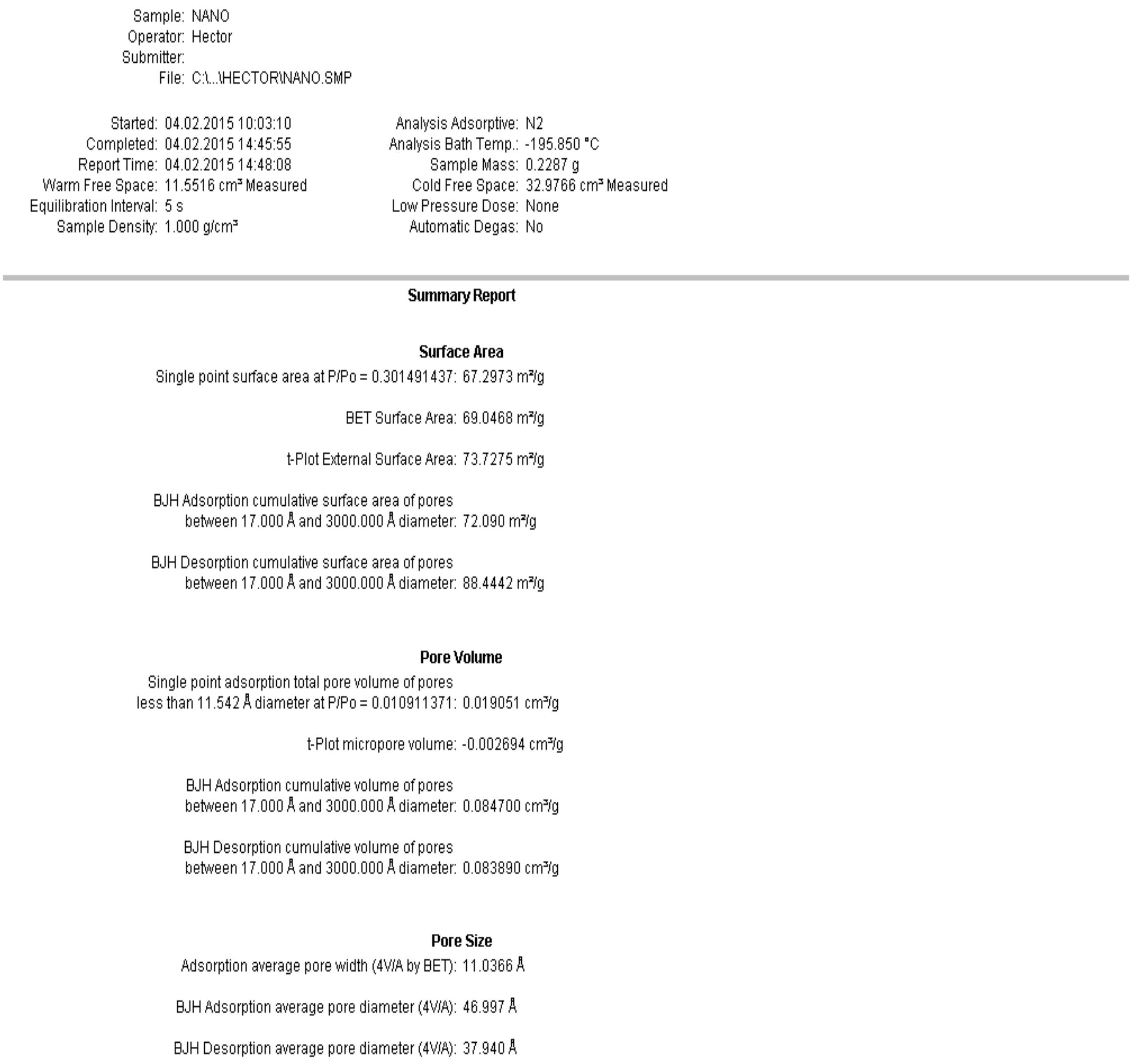
The MicroGC measured the hydrogen outlet flow in cycles that lasted around 5 minutes.

The liquid inside the reactor experienced a colour change after a few minutes of exposure to the UV light.

3. RESULTS AND DISCUSSION

1 NANOTUBES SYNTHESIS

After the hydrothermal synthesis and the washing process using centrifugation, the BET technique was used to measure the surface area of the product and check the correct formation of nanotubes. The BET analysis results were the following:



```
              Sample:  NANO
            Operator:  Hector
           Submitter:
                File:  C:\...\HECTOR\NANO.SMP

             Started:  04.02.2015 10:03:10            Analysis Adsorptive:  N2
           Completed:  04.02.2015 14:45:55          Analysis Bath Temp.:  -195.850 °C
         Report Time:  04.02.2015 14:48:08                  Sample Mass:  0.2287 g
    Warm Free Space:  11.5516 cm³ Measured             Cold Free Space:  32.9766 cm³ Measured
Equilibration Interval:  5 s                          Low Pressure Dose:  None
      Sample Density:  1.000 g/cm³                     Automatic Degas:  No

                                   Summary Report

                                    Surface Area
        Single point surface area at P/Po = 0.301491437:  67.2973 m²/g

                                        BET Surface Area:  69.0468 m²/g

                               t-Plot External Surface Area:  73.7275 m²/g

        BJH Adsorption cumulative surface area of pores
              between 17.000 Å and 3000.000 Å diameter:  72.090 m²/g

        BJH Desorption cumulative surface area of pores
              between 17.000 Å and 3000.000 Å diameter:  88.4442 m²/g


                                    Pore Volume
       Single point adsorption total pore volume of pores
    less than 11.542 Å diameter at P/Po = 0.010911371:  0.019051 cm³/g

                                 t-Plot micropore volume:  -0.002694 cm³/g

              BJH Adsorption cumulative volume of pores
              between 17.000 Å and 3000.000 Å diameter:  0.084700 cm³/g

              BJH Desorption cumulative volume of pores
              between 17.000 Å and 3000.000 Å diameter:  0.083890 cm³/g


                                     Pore Size
              Adsorption average pore width (4V/A by BET):  11.0366 Å

               BJH Adsorption average pore diameter (4V/A):  46.997 Å

               BJH Desorption average pore diameter (4V/A):  37.940 Å
```

The commercial P-25 TiO_2 used to prepare the nanotubes had a surface area of 50 m2/g. The BET surface area of the nanotubes found in the Literature for this synthesis method was ranging from 100 to 478 m2/g.

The main explanation that can be given to the value of 69 m2/g for the surface area of the nantubes (which was less than the expected), is that the washing process that was used did not favour the nanotubes formation.

Before the washing, lamellar sheets are formed during the hydrothermal process; but the washing treatment removes the electrostatic repulsion and results in the formation of the nanotube structure.

In these experiences, a washing process without using HCl was chosen. Since the use of the hydrochloric acid was already researched and documented, and removing the NaCl from the powder could add some complications, a repetitive water washing was chosen instead. It’s very likely that this neutralization process using only water to eliminate the NaOH, could have affected the electrostatic repulsion removing process, and the nanotube structure formation.

Another explanation is that the hydrothermal synthesis procedure requires a strict control of the temperature in the solution and the heated bath that was used to keep the matrass at 110ºC experienced some temperature fluctuations and proved not to be the ideal temperature controller for this kind of process. These fluctuations in temperature could have led to partial nanotube formation.

The first washing filtration procedure that was tried (described in the annexes) led to substantial losses of powder and even worst results so it was discarded as a suitable method for obtaining the nanotubes.

It must be suggested that for further research on the subject, a different synthesis method could be used to obtain the nanotubes, such as electrochemical anodization or atomic layer deposition and compare the results obtained.

In most of the publications an autoclave was used for the nanotubes formation and washing, which allowed a perfect control over the temperature at any given time.

Square chamber Autoclave

The hydrothermal synthesis time was of 48 hours. Most of the literature consulted stated that the synthesis time needed to be at least of 20 hours, so the time expended on the synthesis is not a reason to explain the lower surface area of the Nanotubes.

2 REACTION

As the synthesis of the catalyst took most of the time available for the project, only one parameter could be tested in the reaction.

It was decided that the Copper loading was going to remain constant at 5 % of the catalyst mass, and the reactant solution was set at 50% vol MeOH and 50% vol distilled water. The wavelength of the UV radiation in every experience was UVC and the carrier gas of the MicroGC was Argon.

Therefore the only parameter that was changed in the reactions was the total mass of the catalyst in the reactor. The experienced varied that parameter starting with a load of 250 mg (which was the optimal found in the literature), and following with 200mg, 150mg, 100mg and finally 300mg.

The hydrogen production observed in the different reactions was limited to some traces measured by the MicroGC. It revealed when hydrogen was started to be produced but however, it was a very small flow and couldn't be quantified.

In some of the experiences no hydrogen production at all could be detected by the chromatographer.

250mg Catalyst mass.

This experience had to be repeated because the first time it was run, no hydrogen production was observed. This could be caused by a leakage in the reactor, and the fact that the set up had been out of use during a whole semester and some detection problems could be present in the Chromatographer.

In the second run of the reaction, better results were obtained.

After 8 hours of reaction time, the MicroGC started to detect hydrogen production. The traces continued to be detected during the whole reaction time from that point until the reaction was stopped after 20 hours and 30 minutes.

In this experience an early colour change in the reaction mix was detected after only 15 minutes. The liquid in the reactor turned to a darker colour after a short exposure to the UVC light.

200mg Catalyst mass

For this catalyst mass, the results were similar to the last experience.

This time hydrogen traces were not observed until 14 hours and 15 minutes of reaction time. Hydrogen continued to be produced in that way until the reaction was stopped after 23 hours and 9 minutes.

The same change in the colour of the reactant liquid was experienced after 15 minutes of exposure to the UVC light.

150mg Catalyst mass

In the experience with this amount of catalyst the results were slightly different.

No hydrogen production evidence was found in the first 9 hours of reaction. But after 9 hours and 47 minutes, hydrogen traces were detected by the chromatographer.

In the next 2 hours the detector didn’t registered any traces of hydrogen until 12 hours and 28 minutes of reaction, when the traces were detected again.

The next hour didn’t register any hydrogen production and after that at; 14 hours and 15 minutes it started to be registered again. The measurement only recorded traces until the reaction was stopped after 22 hours and 16 minutes.

At the end of the reaction the liquid had the same colour change that happened in the previous experiences.

100mg Catalyst mass

During all the reaction time no hydrogen was detected by the MicroGC.

The reaction was stopped after 22 hours and 17 minutes. The same colour change in the liquid happened in this experience; however, since the catalyst amount in the sample was smaller, the intensity of the colour was less intense.

300mg Catalyst mass

In this last experience no hydrogen production was detected along the reaction time.

The reaction was run for 23 hours and 7 minutes with no production detected by the MicroGC. The colour change present in the other experiences happened in this one as well, being even more drastic due to the bigger amount of powder in the reactor.

CONCLUSIONS

Given the results obtained, the best statements that should be made concern the Nanotubes synthesis.

As is reflected both in the results of the BET analysis and those of the reactions, it seems obvious that only a partial nanotube formation was achived. This is attributed mostly to the chosen washing procedure. Even though special care was taken to neutralize the ph until it reached the level of 7 using distilled water, some publications suggest that the effect of the HCl in the removing of the electrostatic repulsion charges and the transition between the lamellar sheets and the nanotubes is of great importance. However the process of nanotube formation is still in research and not all the steps in the transformation can be explained yet.

It was previously stated that the temperature was a critical factor during the hydrothermal synthesis and it should remain constant during the nanotube formation.

The heated bath and the refrigeration column provided the needed temperature (110º) for the NaOH solution to reach the bubble point and the stirring mechanism was efficient enough to keep the TiO2 particles equally distributed along the solution in the recipient. However the temperature was not stable enough and some fluctuations occur. The Silicon oil used in the bath was not stirred and probably the temperature was not uniform inside the container.

Regarding the reaction part, the low hydrogen production results can be attributed to different reasons.

One of the first possible causes is the deterioration of the sealing mechanism of the lid in the reactor. The exposure to UV radiation affects the properties of rubber and can produce small leaks in the sealing band and the joints for the inlet and the outlet. Those kind of leaks, given the very low hydrogen production in this kind of reactions, leads to a very low concentration of hydrogen been dragged through the outlet of the reactor to the chromatographer.

Another factor that should be considered is the amount of time that the MicroGC had been out of use before the reactions (around 7 months). This is revealed in the first reaction that was tried, which didn't give any hydrogen production at the first try, but give some traces at the second place.

The general limitation in the Hydrogen production seems to be a conversion limitation and not a selectivity one. This is explained as it doesn't seem to be any relevant secondary reaction on the reactor mix, no other gasses apart from Hydrogen are detected in the chromatographer, and the methanol in the mix remains unchanged after the reaction.

With the kind of results that were obtained is difficult to make an statement about the optimization of the catalyst mass parameter, but it seems like the 300 mg and the 100 mg experiences were the border of the optimal zone for the reaction as those were the only ones that didn’t give any hydrogen production and both were either the top limit or the bottom limit of the effective mass of catalyst.

The 250mg experience was the one that started to produce the traces of hydrogen at an early stage in a continuous pattern, so that would qualify that catalyst mass as the most efficient of the ones that were experimented with, under the given conditions of reactant concentration, wavelength of the radiation, alcohol selected and copper loading in the catalyst among others.

Without having numbers for the hydrogen production in the different reactions there’s no enough data to establish any further conclusions about the optimization of the parameters.

FUTURE PROSPECTS

After the results obtained in the experiences of this project, the following lines of investigation should be investigated for further research on the subject.

- Effective temperature and ph control during the synthesis of the nanotubes will lead to better results and a higher surface area on the structures synthesised
- Alternative synthesis methods for the nanotube formation such as electrochemical anodization or atomic layer deposition should be tried and compared.
- Other washing procedures should be investigated, in order to neutralize the nanotube powder and proper formation of the nanotub structure. The centrifugation method worked better than the vacuum filtration, but the addition of HCl to the washing process could lead to better results.
- The use of different alcohols and different concentrations of them in the reacting mix should be documented and optimized.
- The Copper loading of the catalyst should be changed to bigger and lower percentages and record the effect on the hydrogen production. This parameter should be optimised when the others remain constant.
- Other wavelengths in the UV spectre should be tried in the reaction, and detect which is the optimal wavelength when other parameters remain constant.
- Other metal conductors should be researched for the coating of the TiO2 nanotubes, and the results should be compared.
- Measuring the methanol concentration at some points during the reaction could give a better understanding of the reaction process, and help to discover the possible secondary reactions that can be present in the process.
- The colour change in the reaction mix after a few minutes of exposure to the UV radiation should be researched, and measured in order to find out the cause of this phenomenon.

REPRODUCIBILITY

In order to have coherent results that could be used to reach some conclusions on the field and to be used in further research, reproducibility was a very important factor to take into account.

In every stage of the experimental process a special care was taken into having the same conditions for the procedures that were being made. This ensured that every batch of the catalyst synthesised and arranged for the reaction had the same properties and followed the same process.

The most remarkable aspects of the reproducibility in the experiments are:

- The amount of P-25 $TiO2$ powder used for the hydrothermal nanotube synthesis was always the same, as well as the volume and concentration of the NaOH solution.

- The same graduated cylinder and lab material was used for the same operations

- The same centrifugation sample tubes were used for the washing process.

- The position of the reactor in the reactor container was marked to be repeated in every experience

- The same magnetic stirrer was used for all the reactions, and the same speed was used.

SYMBOLS AND NOMENCLATURE

MeOH – Methanol

Rpm - Rounds per minute

MicroGC – Micro Gas Chromatographer

XRD – X-Ray Diffraction

SEM – Scanning Electron Microscopy

UV- Ultraviolet radiation

D – Donor

A – Acceptor

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APPENDIX

1.- COLOUR CHANGE IN THE SAMPLE

After the first 15 minutes of reaction, a colour change could be observed in the liquid inside the reactor. Before been exposed to the UV light, the reaction mix had a light green/white colour; however, after a few minutes of exposer to UV light the colour changed to a darker green.

Reaction liquid before been exposed to UV light.

Reaction liquid after the UV exposure.

The liquid also experienced an odour change along with the colour. In the initial liquid mix only a slight methanol smell could be perceived; however, after the reaction a rotten-like odour was perceived. That could indicate that other gas products were being produced apart from hydrogen; however they must be produced in small amount, as they are not detected by the chromatographer.

2.- VACUUM FILTRATION WASHING PROCEDURE

Before starting to use centrifugation in the washing treatment following the hydrothermal synthesis, vacuum filtration using a Büchner funnel was carried out.

The venture effect was used to produce a vacuum in the Büchner funnel and the filtering paper, and the solution was washed several times using distilled water until the ph was neutralized and reached a value of 7.

Detail of the Venturi effect vacuum device.

Büchner funnel with the filtering paper.

The experimental procedure consisted in slowly pouring the solution with the TiO_2 nanotubes on the Büchner funnel while the vacuum was activated and refilling the funnel several times with distilled water.

The liquid exiting the funnel had to be ph tested until it reached a level of seven. Then the filtering paper with the TiO_2 nanotubes was extracted from the funnel and let to dry at 60º in the oven. After that the powder was collected and stored, before proceding with the next step which was the Incipient Wetness Impregnation to coat the powder with Copper.

Filtering-Washing set up.

This method led to a great powder loss and proved to be inefficient. The high ph of the NaOH solution usually damaged the filtering paper and no filtration was produced.

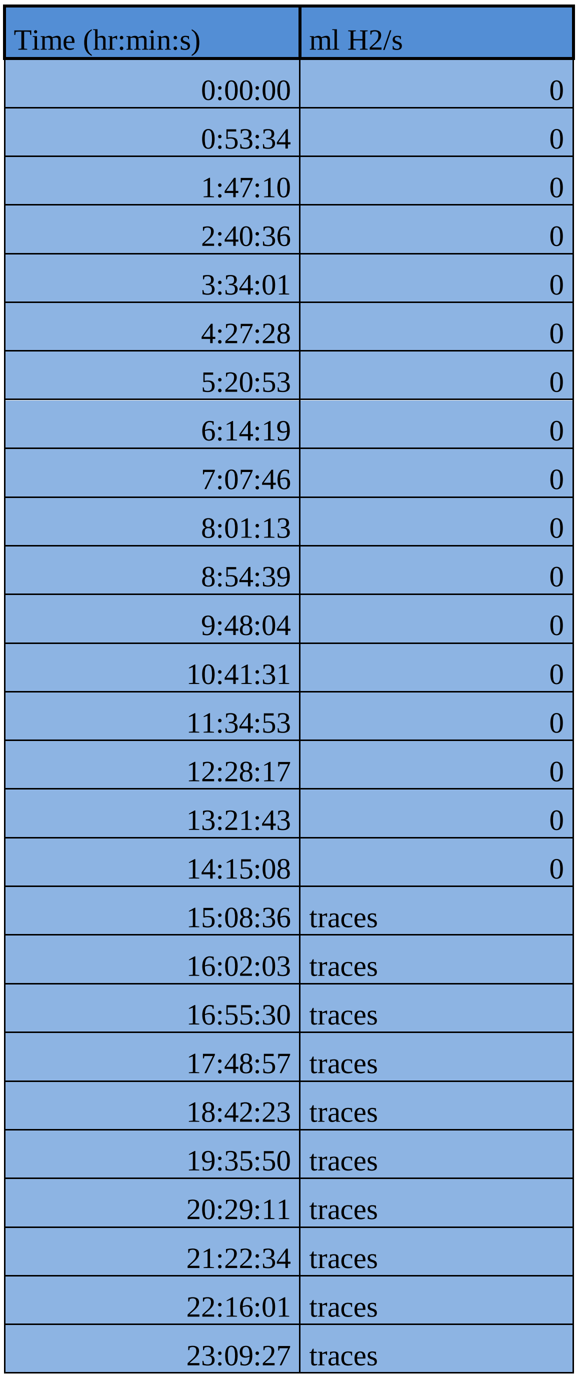
The separation of the powder from the filtering paper was also problematic and led to contamination of the sample with paper and significant amount of powder not being able to be separated.

3.- DATA FOR THE REACTION HYDROGEN PRODUCTION

250mg catalyst mass

Time (hr:min:s)	ml H2/s
0:00:00	0
0:53:27	0
1:46:52	0
2:40:19	0
3:33:45	0
4:27:09	0
5:20:37	0
6:14:05	0
7:07:31	0
8:01:03	0
8:54:40	traces
9:48:07	traces
10:41:32	traces
11:34:59	traces
12:28:26	traces
13:21:55	traces
14:15:29	traces
15:09:05	traces
16:02:44	traces
16:56:24	traces
17:49:51	traces
18:43:17	traces
19:37:29	traces
20:30:10	traces

200mg Catalyst mass



Time (hr:min:s)	ml H2/s
0:00:00	0
0:53:34	0
1:47:10	0
2:40:36	0
3:34:01	0
4:27:28	0
5:20:53	0
6:14:19	0
7:07:46	0
8:01:13	0
8:54:39	0
9:48:04	0
10:41:31	0
11:34:53	0
12:28:17	0
13:21:43	0
14:15:08	0
15:08:36	traces
16:02:03	traces
16:55:30	traces
17:48:57	traces
18:42:23	traces
19:35:50	traces
20:29:11	traces
21:22:34	traces
22:16:01	traces
23:09:27	traces

150mg Catalyst mass

Time (hr:min:s)	ml H2/s
0:00:00	0
0:53:23	0
1:46:49	0
2:40:18	0
3:33:45	0
4:27:11	0
5:20:38	0
6:14:04	0
7:07:31	0
8:00:59	0
8:54:25	0
9:47:51	traces
10:41:18	0
11:34:48	0
12:28:29	traces
13:21:57	0
14:15:24	traces
15:08:49	traces
16:02:15	traces
16:55:43	traces
17:49:08	traces
18:42:35	traces
19:36:01	traces
20:29:27	traces
21:22:53	traces
22:16:14	traces

300mg Catalyst mass

Time (hr:min:s)	ml H2/s
0:00:00	0
0:53:23	0
1:46:46	0
2:40:09	0
3:33:32	0
4:26:55	0
5:20:18	0
6:13:41	0
7:07:04	0
8:00:27	0
8:53:50	0
9:47:13	0
10:40:36	0
11:33:59	0
12:27:22	0
13:20:45	0
14:14:08	0
15:07:31	0
16:00:54	0
16:54:17	0
17:47:40	0
18:41:03	0
19:34:26	0
20:27:49	0
21:21:12	0
22:14:35	0
23:07:58	0

100mg Catalyst mass

Time (hr:min:s)	ml H2/s
0:00:00	0
0:53:29	0
1:46:58	0
2:40:27	0
3:33:56	0
4:27:25	0
5:20:54	0
6:14:23	0
7:07:52	0
8:01:21	0
8:54:50	0
9:48:19	0
10:41:48	0
11:35:17	0
12:28:46	0
13:22:15	0
14:15:44	0
15:09:13	0
16:02:42	0
16:56:11	0
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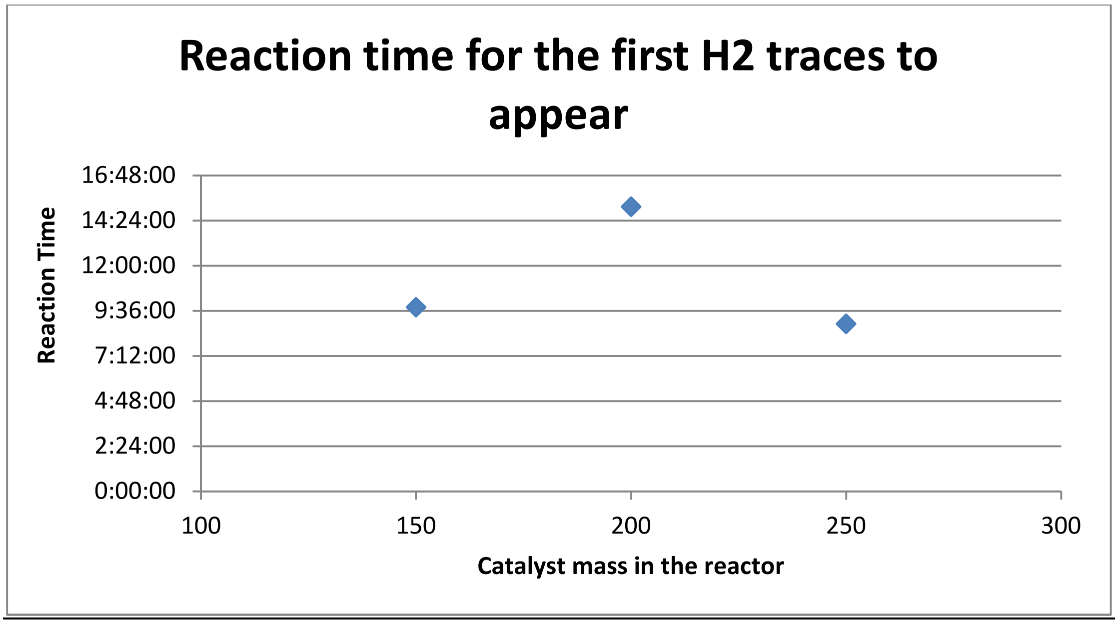
20:30:07	0
21:23:36	0
22:17:05	0


Reaction time for the first H2 traces to appear
Reaction Time
16:48:00
14:24:00
12:00:00
9:36:00
7:12:00
4:48:00
2:24:00
0:00:00
100
150
200
250
300
Catalyst mass in the reactor

4.- CALIBRATION OF THE ARGON FLOW TO THE REACTOR

In the line that introduces Argon in the reactor there is a valve that can be regulated to allow different flows of Argon. That valve has to be calibrated using a bubble flow meter present in a secondary line, establishing a relation between the opening percentage, and the actual Argon flow in the line

The calibration of that valve was done by setting the valve at 5 different percentages of aperture, and for each of them 5 measurements of the flow were done. To measure the flow, some soap bubbles where introduced into the bubble flowmeter. The flowmeter had a mark for 1 ml and another one for 10 ml. The measurements were taken checking the time that it took one bubble to flow from the 1 ml mark to the 10 ml mark with a chronometer.

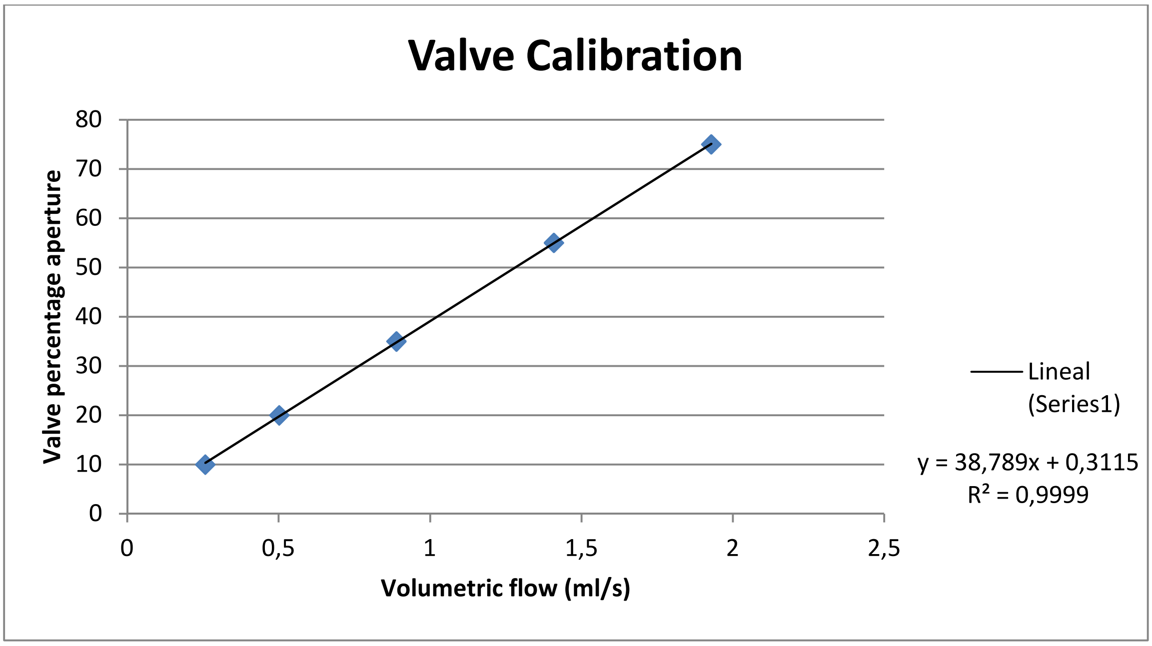
Bubble Flowmeter used for the calibration of the valve

With 5 time measurements per each valve position, the average was calculated; and then the flow in ml/s.

The data for the volumetric flow was plotted versus the percentage of valve aperture, and then the linear regression was calculated. Knowing the slope of the linear regression, the equation for that line was calculated and use to guess which valve aperture would correspond to a flow of 10 ml/min.

% opening/time (s)1-10ml	75%	55%	35%	20%	10%
1º time (s)	4,95	6,28	10,09	17,94	34,34
2º time (s)	4,69	6,22	10,18	17,88	34,93
3º time (s)	4,66	6,60	10,03	17,87	35,15
4ºctime (s)	4,47	6,44	10,00	17,81	35,09
5º time (s)	4,56	6,40	10,30	18,11	35,06
Average(s)	4,67	6,39	10,12	17,92	34,91
V flow(ml/s)	1,93	1,41	0,89	0,50	0,26

Table with experimental data for the calibration of the valve



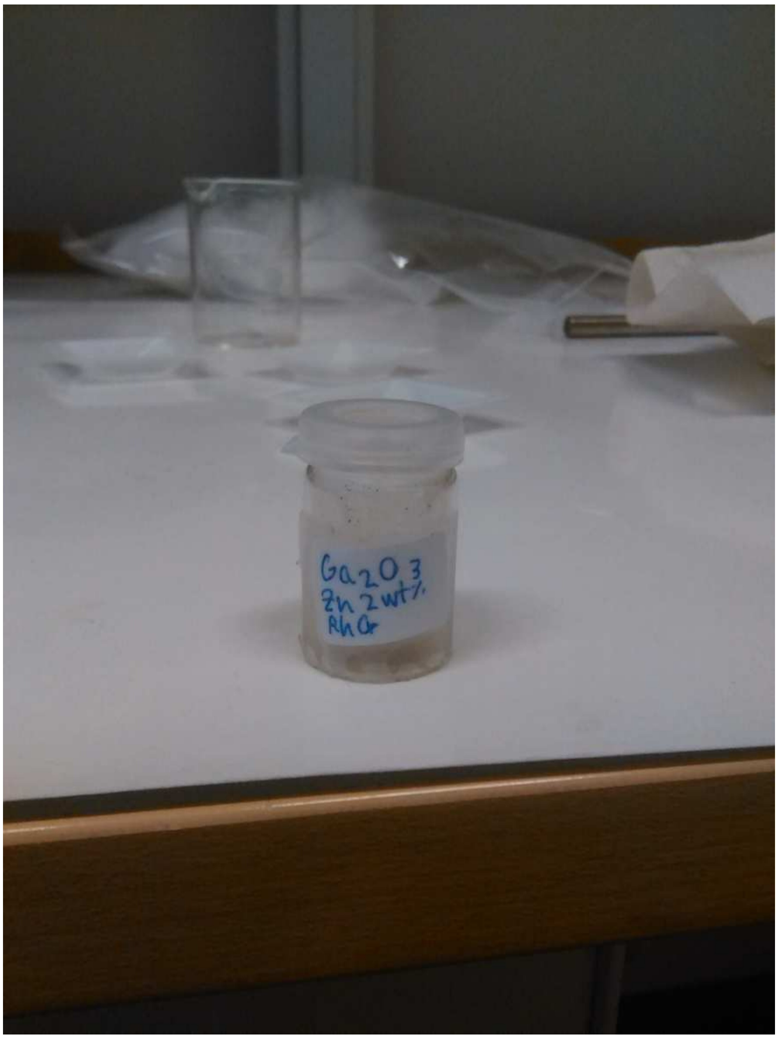
Graphic with the linear regression of the experimental data.

Introducing the value of 10 ml/min (0,167ml/s) in the equation of the linear regression, the valve opening calculated was 6.5 %; which was the one used in all the photocatalytic reactions.

5.- EXPERIMENT WITH THE SAMPLE FROM THE UNIVERSITY OF TARRAGONA

A sample of a photocatalyst from the University of Tarragona (Spain) was tested in the photoreactor under the same conditions as the reactions of this project.

The catalyst sample was Ga_2O_3 coated with 2% w/w Zn. And 250mg of this powder were added to the reactor with a 500 ml reaction mix consisting in 250ml of MeOH and 250ml of distilled water.



Catalyst Sample.

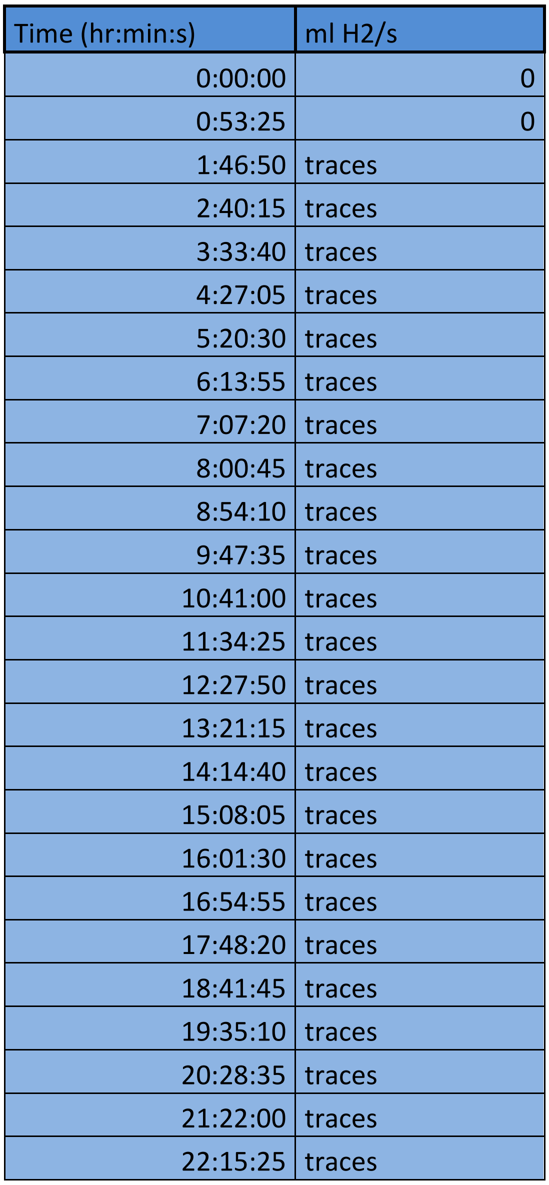
The lamps were set at UVC light wavelength and the reactor was placed inside the reactor container.

Before switching the lights on and starting the MicroGC software, tha same 30 min ventilation with Argon as the one for the TiO2 nanotube catalyst was done. The valve for the Argon flow was set at 100% aperture and the stirring was activated.

After that, the flow was set to 10 ml/min (6.5% valve aperture), the lamps were switched on and the MicroGC software initiated, starting the reaction.

The results obtained indicated that hydrogen was produced in an early stage of the reaction (after 1 hour and 46 minutes) and kept being produced until the reaction was stopped after 22 hours and 15 minutes.

However, the hydrogen produced was not enough to be quantified by the MicroGC, and only traces were measured. That allowed to state that the catalyst had a low activity, but faster response than the main catalyst tested in the project.



Time (hr:min:s)	ml H2/s
0:00:00	0
0:53:25	0
1:46:50	traces
2:40:15	traces
3:33:40	traces
4:27:05	traces
5:20:30	traces
6:13:55	traces
7:07:20	traces
8:00:45	traces
8:54:10	traces
9:47:35	traces
10:41:00	traces
11:34:25	traces
12:27:50	traces
13:21:15	traces
14:14:40	traces
15:08:05	traces
16:01:30	traces
16:54:55	traces
17:48:20	traces
18:41:45	traces
19:35:10	traces
20:28:35	traces
21:22:00	traces
22:15:25	traces

Reaction Data for the sample from Tarragona

The same change of odour as in the other experiences was present after the reaction in the liquid, but the colour change was slighter than in the other experiments and the liquid turned to a light orange colour.

Liquid before the reaction.

Reaction liquid after the experiment.

6.- XRD ANALYSIS OF A Au-TiO_2 SAMPLE

A sample of a TiO_2 gold-coated catalyst was analysed by X-ray Diffraction.

The thin powder was poured in one of the small XRD sample holders and was soaked with ethanol and flattened to the surface of the metal part of the holder. Then it was left to dry for 24 hr.

XRD sample holder with the catalyst powder.

When the analysis was being made, the sample holder was set on the sample port of the D-8 Focus X-ray diffractometer.

Using the software, the starting and finishing angle of incidence of the beam was selected, as well as the step angle between different cycles in measurements. After introducing all the information needed for the run, the analysis started.

D8 Focus X-Ray Diffractometer

XRD analysis in process.

After the analysis was completed, the software plotted the peaks found during the process vs. the diffraction angle. Then, using the database, the peaks were checked and compare to the crystalline structures in the archive, filtering the matches only checking the interesting atomic elements.

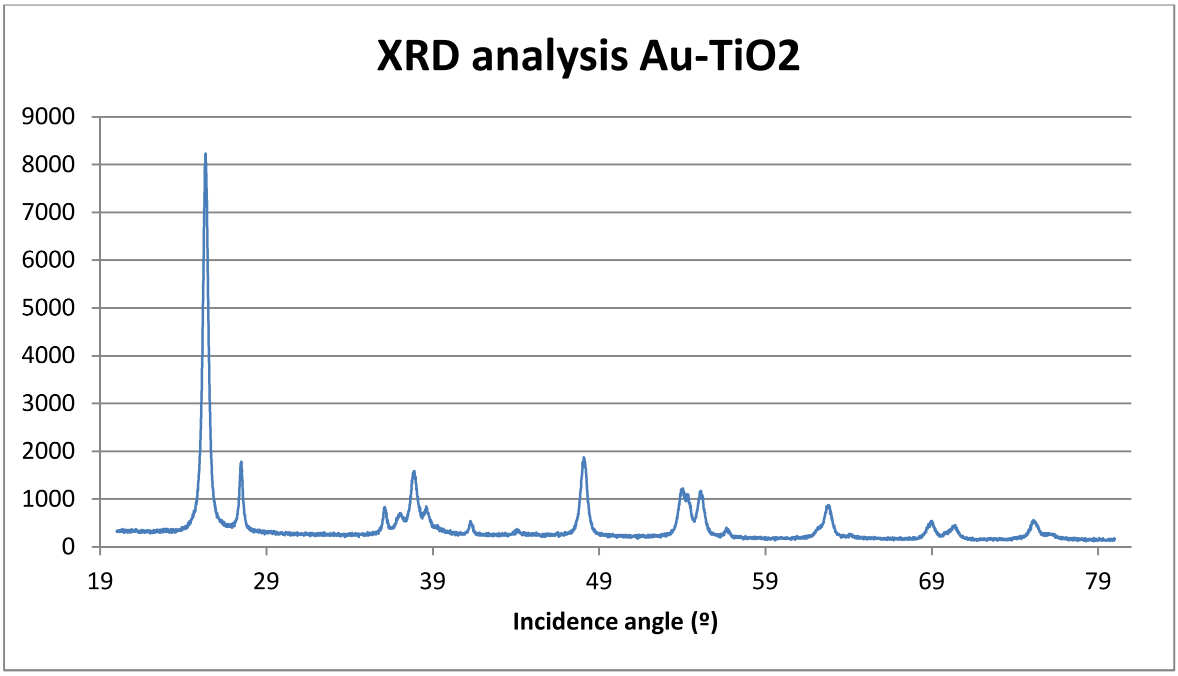
The results obtained revealed that the main structure of the powder was Rutile and Anatase, and Gold.

Reduced Data table for the XRD analysis.

angle(º)	intensity
20	327
21,0136	320
22,0129	282
23,0122	314
24,0115	407
25,0108	1999
26,0101	715
27,0094	499
28,0087	389
29,008	326
30,0073	250
31,0066	269
32,0059	256
33,0053	241
34,0046	239
35,0039	246
36,0032	591
37,0025	641
38,0018	1310
39,0011	452

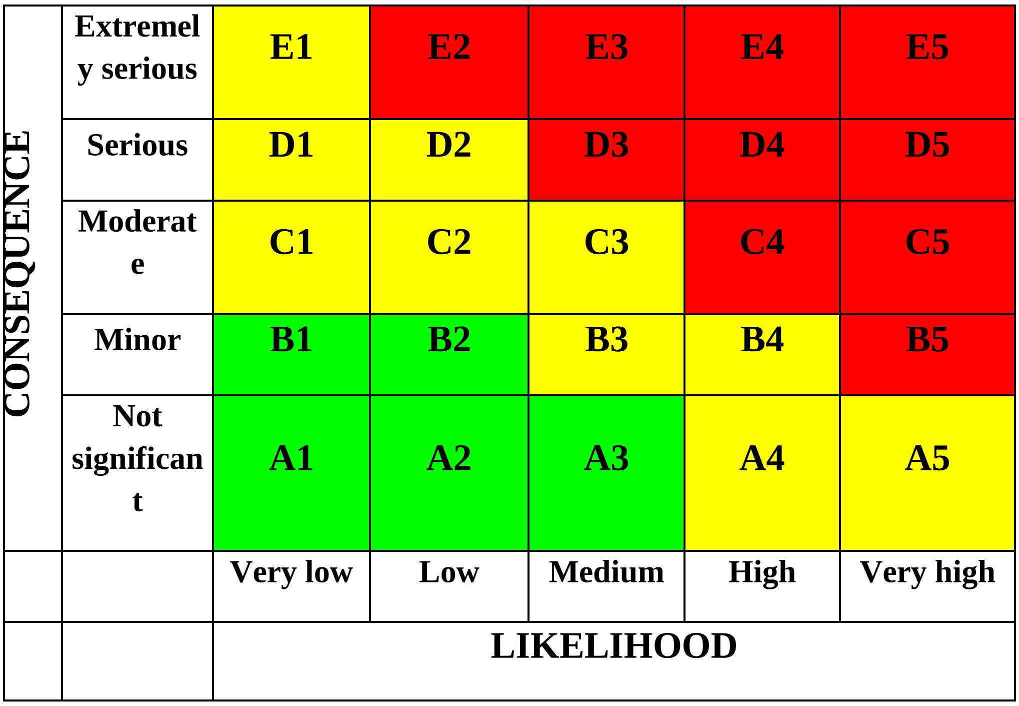
angle(º)	intensity
40,0004	307
41,014	318
42,0133	271
43,0126	244
44,0119	333
45,0112	243
46,0105	251
47,0098	296
48,0091	1769
49,0084	266
50,0077	208
51,007	224
52,0063	241
53,0056	215
54,005	1212
55,0043	1000
56,0036	267
57,0029	240
58,0022	187
59,0015	185

angle(º)	intensity
60,0008	196
61,0001	176
62,0137	320
63,013	567
64,0123	199
65,0116	181
66,0109	173
67,0102	167
68,0095	182
69,0088	535
70,0081	336
71,0074	163
72,0067	147
73,006	159
74,0054	190
75,0047	454
76,004	280
77,0033	162
78,0026	158
79,0019	146
80,0012	165



Graph of the XRD peaks obtained.

7.- MATRIX FOR RISK ASSESSMENTS



CONSEQUENCE	**Extremely serious**	**E1**	**E2**	**E3**	**E4**	**E5**
	Serious	**D1**	**D2**	**D3**	**D4**	**D5**
	Moderate	**C1**	**C2**	**C3**	**C4**	**C5**
	Minor	**B1**	**B2**	**B3**	**B4**	**B5**
	Not significant	**A1**	**A2**	**A3**	**A4**	**A5**
		Very low	**Low**	**Medium**	**High**	**Very high**
		LIKELIHOOD				

Principle for acceptance criteria. Explanation of the colours used in the risk matrix.

Colour		**Description**
Red	🟥	Unacceptable risk. Measures must be taken to reduce the risk.
Yellow	🟨	Assessment range. Measures must be considered.
Green	🟩	Acceptable risk Measures can be considered based on other considerations.

Potential undesirable incident/strain

Identify possible incidents and conditions that may lead to situations that pose a hazard to people, the environment and any materiel/equipment involved.

Criteria for the assessment of likelihood and consequence in relation to fieldwork

Each activity is assessed according to a worst-case scenario. Likelihood and consequence are to be assessed separately for each potential undesirable incident.

Before starting on the quantification, the participants should agree what they understand by the assessment criteria:

Likelihood

Minimal 1	Low 2	Medium 3	High 4	Very high 5
Once every 50 years or less	Once every 10 years or less	Once a year or less	Once a month or less	Once a week

Consequence

Grading	Human	Environment	Financial/material
E Very critical	May produce fatality/ies	Very prolonged, non-reversible damage	Shutdown of work >1 year.
D Critical	Permanent injury, may produce serious serious health damage/sickness	Prolonged damage. Long recovery time.	Shutdown of work 0.5-1 year.
C Dangerous	Serious personal injury	Minor damage. Long recovery time	Shutdown of work < 1 month
B Relatively safe	Injury that requires medical treatment	Minor damage. Short recovery time	Shutdown of work < 1week
A Safe	Injury that requires first aid	Insignificant damage. Short recovery time	Shutdown of work < 1day

The unit makes its own decision as to whether opting to fill in or not consequences for economy/materiel, for example if the unit is going to use particularly valuable equipment.

It is up to the individual unit to choose the assessment criteria for this column.

Risk = Likelihood x Consequence

Please calculate the risk value for “Human”, “Environment” and, if chosen, “Economy/materiel”, separately.

About the column ”Comments/status, suggested preventative and corrective measures”: Measures can impact on both likelihood and consequences. Prioritise measures that can prevent the incident from occurring; in other words, likelihood-reducing measures are to be prioritised above greater emergency preparedness, i.e. consequence-reducing measures.

Unit: CED (Chemical Engineering Department) **Date: 19.02.2015**

Participants in the identification process (including their function): Héctor Iglesias (student), Magnus Rønning (supervisor)

Short description of the main activity/main process: Synthesis of the catalyst.

ID no.	Activity/process	Responsible person	Existing documentation	Existing safety measures	Laws, regulations etc.	Comment
A1	P25 TiO_2 Handling	Magnus Rønning	Material Safety Data Sheet	Fume Hood	AML 4-5, HMSRV-12/13, HMSR-39, HMSR-40, Chemical Regulations	Safety Googles, Gloves
A2	Copper Nitrate Handling	Magnus Rønning	Material Safety Data Sheet	Fume Hood	AML 4-5, HMSRV-12/13, HMSR-39, HMSR-40, Chemical Regulations	Safety Googles, Gloves
A3	Calcination	Magnus Rønning	Manuals	Fume Hood	AML 4-5, HMSRV-12/13, HMSR-39, HMSR-40, Chemical Regulations	Safety Googles, Thermal Gloves
A4	Addition NaOH (nanotubes preparation)	Magnus Rønning	Material Safety Data Sheet	Fume Hood	AML 4-5, HMSRV-12/13, HMSR-39, HMSR-40, Chemical Regulations	Safety Googles, Gloves

Unit: CED (Chemical Engineering Department) **Date: 19.02.2015**

Participants in the identification process (including their function): Héctor Iglesias (student), Magnus Rønning (supervisor)

Short description of the main activity/main process: Photoreaction of Methanol and calibration.

ID no.	Activity/process	Responsible person	Existing documentation	Existing safety measures	Laws, regulations etc.	Comment
B1	Activity measurements UV	Magnus Rønning	Material Safety Data Sheet	UV Protection Googles	HMSR-32, Radiation regulation, manuals, Procedures	
B2	Measuring Methanol	Magnus Rønning	Material Safety Data Sheet	Fume Hood	AML 4-5, HMSRV-12/13, HMSR-39, HMSR-40, Chemical Regulations	Safety Googles, Gloves
B3	Calibration of MicroGC and reactivation of Catalyst (Hydrogen)	Magnus Rønning	Material Safety Data Sheet	Individual Gas detectors	AML 4-5, HMSRV-12/13, HMSR-39, HMSR-40, Chemical Regulations	

Unit: CED (Chemical Engineering Department) **Date: 19.02.2015**

Participants in the identification process (including their function): Héctor Iglesias (student), Magnus Rønning (supervisor)

Short description of the main activity/main process: Characterization of Catalyst

ID no.	Activity/process	Responsible person	Existing documentation	Existing safety measures	Laws, regulations etc.	Comment
C1	Chemisorption with hydrogen	Magnus Rønning	Material Safety Data Sheet	Leak test, Gas detectors, Closed fume hoods	AML 4-5, HMSRV-12/13, HMSR-39, HMSR-40, Chemical Regulations	
C2	Pulse chemisorption with N_2O	Magnus Rønning	Material Safety Data Sheet	Leak test, gas detectors, closed fume hoods	AML 4-5, HMSRV-12/13, HMSR-39, HMSR-40, Chemical Regulations	

Unit: **CED (Chemical Engineering Department)** **Date:** **19.02.2015**

Line manager:

Participants in the risk assessment (including their function): Héctor Iglesias (student), Magnus Rønning

ID no.	**Activity from the identification process form**	**Potential undesirable incident/strain**	**Likelihood:**	**Consequence:**				**Risk value Human**	**Comments/status Suggested measures**
			Likelihood (1-5)	**Human (A-E)**	**Environment (A-E)**	**Economy/ material (A-E)**	**Reputation (A-E)**		
A1	P25 TiO2 Handling	Contact with the dust (airways)	1	B				B1	Use gloves and avoid contact with airways
A2	Copper Nitrate Handling	Contact with the skin and eyes.	2	B				B2	Use gloves and avoid contact with airways
A3	Calcination	Burns and gas leaks	2	C				C2	Wait for cooling down, use thermal gloves.
A4	Addition NaOH (nanotubes preparation)	Contact with skin and eyes	2	B				B2	Googles, Gloves and lab Coat
B1	Activity measurements UV	Exposure to UV radiation	5	A				A5	minimiza the exposition, and use UV protection googles
B2	Measuring Methanol	Contact with the skin and eyes.	3	A				A3	Googles, Gloves and lab Coat
B3	Calibration of MicroGC and reactivation of Catalyst (Hydrogen)	Gas leak (can lead to explosion)	1	D				D1	Leak test and gas Detectors should be used
C1	Chemisorption with hydrogen	Gas leak (can lead to explosion)	1	D				D1	Leak test and gas Detectors should be used
C2	Pulse chemisorption with N2O	Gas leak (Asphyxia and Anaesthetic effect)	1	C				C1	Leak test

Likelihood, e.g.:

1. *Minimal*
2. *Low*
3. *Medium*
4. *High*
5. *Very high*

Consequence, e.g.:

A. Safe
B. Relatively safe
C. Dangerous
D. Critical
E. Very critical

Risk value (each one to be estimated separately):
Human = Likelihood x Human Consequence
Environmental = Likelihood x Environmental consequence
Financial/material = Likelihood x Consequence for Economy/materiel