Gold/titania: Synthesis, characterization and photocatalytic performance

Graduation Report
November 2007

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PREFACE

Since 2006 surface interactions and gold are the two themes, which dominate my daily life.

Firstly, surface interactions and chemical reactions on catalyst surfaces are the subject of my MSc graduation project. The importance of this subject was stressed by the Swedish Academy of Sciences last October by awarding Gerhard Ertl the Nobel Prize Chemistry 2007 [0]. His gold medal was earned after years of fundamental studies of the behaviour of molecules at surfaces. I studied the effect of gold on the reactive behaviour of molecules at the surface by depositing gold nanoparticles on catalysts, rendering additional excitement to molecules to improve the chemical reaction.

Secondly, surface interactions and gold play an important role in my personal life too. I try to realize a dream, which started when I began rowing in the 2nd year of my education. The dream to win the gold medal during the Olympics in Beijing in 2008. Rowing is a sport where, as in catalysis, interactions determine the success. Interactions between water, boat, oars and human beings are the key for winning gold. This gold is the catalyst to remain motivated and to invest more than 30 hours per week in training. Part of the dream has been materialized already last September, when a gold medal was won at the World Rowing Championship in the class Lightweight Eight. Again it has been gold, which gives additional excitement to improve performance as in gold supported catalysis.

Arnoud Greidanus
SUMMARY

In earlier studies at R&CE, TUDelft the photocatalytic oxidation of cyclohexane to cyclohexanone was found to be highly selective towards cyclohexanone, but unfortunately the conversion rate is low due to deactivation of the catalyst.

The aim of this study is to improve the conversion and in the same time to reduce the deactivation of the catalyst during photo oxidation by increasing the oxidation activity on the TiO$_2$ catalyst surface by deposition of metal gold. Metal gold deposition as nanoparticles on the TiO$_2$ surface decreases the electron-hole recombination of the TiO$_2$ semiconductor, resulting in a more efficient charge separation. This better charge separation would improve the photocatalytic activity of the catalyst.

Several TiO$_2$ supports (Degussa P25, Hombicat, Aldrich and Merck) and two different methods for reduction of Au$^{3+}$ to Au$^0$, i.e. calcinations and chemical reduction by NaBH$_4$ were applied.

All catalysts were characterized for specific surface area and for pore distribution by nitrogen physisorption, for active sites by ammonia-TPD, for Au particle size by TEM, for anatase/rutile ratio of TiO$_2$ by RAMAN, XRD, for adsorbed water and OH-groups by TGA and for absorbance capacity of light by UV/VIS.

The Au/TiO$_2$ catalysts were tested on their photocatalytic activity in three different oxidation reactions, namely cyclohexane oxidation to cyclohexanone (liquid-organic oxidation), degradation of methylene blue (liquid-aqueous oxidation) and oxidation of propane and propylene (gas-organic oxidation).

During cyclohexane photo oxidation, high selectivity to cyclohexanone is obtained (cyclohexanone/cyclohexanol 90-97%). For all catalysts the character of the kinetics is very similar. The photo oxidation of cyclohexane follows two reaction stages, an initial stage and a steady-state stage. After an initial stage of 45-60 minutes of illumination the reaction rate decreases significantly. The decrease of reaction rate is attributed to deactivation of the TiO$_2$ catalyst by oxidation of cyclohexanol to carboxylates, which adsorb at the active sites of the catalyst surface. Decarboxylation reactivates the catalyst and is assumed to be the rate determining step in the steady state stage. A two-loop reaction model is proposed to understand the kinetics. Gold deposition of the TiO$_2$ catalysts did not result in higher reaction rates, but in a decrease of both initial as steady state reaction rates. The stronger oxidation activity of Au/TiO$_2$ will increase the kinetics of the cyclohexanol loop of the reaction model. Consequently, oxidation of cyclohexanol leads to accumulation of carboxylates on the catalyst surface. Further research and development of methods, which might speed up the decarboxylation step would be worthwhile for improvement of the photo oxidation rate in the steady state stage.

The kinetics of the decomposition of MB appears to be pseudo first order as well for decomposition with pure TiO$_2$ catalysts as for decomposition with Au/TiO$_2$ catalyst. A two-cycle model is proposed, of
which each cycle has two pathways, one involving a superoxide radical and the other involving an adsorbed hydroxyl ion. The cycles describe the decomposition of MB and the decomposition of MB degradation products respectively. All catalysts show fast decomposition in the initial state at a rate around $3 \cdot 10^{-2}$/min. This rate appears to be independent of the active site concentration. This leads to the conclusion that the adsorption step is the rate determining process of MB decomposition by photo oxidation in the initial state.

The photocatalytic oxidation of MB appears to be a two-stage process, with a decomposition rate in the initial stage, which is a factor 3-8 higher than in the steady state stage. The reduction of this rate is due to the production of degradation products, which compete with MB for absorption sites. In the steady state stage the desorption of degradation products becomes rate limiting.

Pure Hombicat shows an initial delay of MB decomposition, which is explained by the presence of sulphites, which scavenge radicals formed by photo oxidation. After all sulphites are consumed MB decomposition can start.

Gold deposition increased the decomposition rate for Aldrich catalyst only. For Au/Hombicat and Au/P25 the lower rate is believed to be the direct and/or indirect effect of lower active site concentration, in combination with limited diffusivity of MB due to pore diameter restrictions. The significant reduction of active sites could be due to sodium poisoning after the reduction by NaBH$_4$.

Photo oxidation of propane to acetone appears to occur with visible light, although at low conversion rates. Unfortunately, the challenging idea of the possibility of direct photo oxidation of propylene to propylene oxide in the presence of water has a negative outcome. No epoxies are formed, but a lot of other species like acetone, carboxylates and carbonates are detected by FTIR.

In conclusion, the photocatalytic activity could be enhanced by gold deposition. However, competing reactions and catalyst deactivation could have large negative effects on the overall kinetics. As shown in this study, each combination of catalyst, photo oxidation reaction and environment has its own specific limitations. E.g. reaction mechanisms in liquid/gas phase or in aqueous/non-aqueous environment could be different for the same catalyst.

In order to exploit the advantage of high selectivity, each specific photo oxidation process needs to be optimised for catalyst deactivation and competing reactions. Increasing the oxidation activity by gold deposition only is not enough to enhance the kinetics. Some ideas to study are selective active sites by catalyst modification, continuous removal of formed compounds to avoid competing reactions, and reaction medium that contains selective scavengers, which can prevent active sites blockage.
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1. INTRODUCTION

1.1. Catalysis and light.
Nowadays, the use of solar cells for energy supply is the most known application of light acting as the energy source in daily life. Renewable energy is going to be of greater concern the next coming decades due to the predicted shortage of fossil fuels. Last decades the research on solar cells is increased tremendously, which resulted in improvement of the efficiency and costs [1].

Photolysis (in Greek: breakdown by light) is a very old process that exists since the beginning of earth (splitting of water) and is nowadays applied in chemical engineering also. Light can also be used as an energy source in electrolysis where a solar cell (semiconductor) adsorbs light and converts the energy of the photons to electricity. Electrons are running through the electric circuit to create the electrolyse process. However, it is also possible to introduce this semiconductor directly into the reaction medium. In this case, the semiconductor is called a photo-catalyst and the energy of photons is converted via electronic shifting into chemical energy. As in solar cells, this process of electronic shifting in a semiconductor is called the photovoltaic effect. The catalytic activity of a semiconductor can be described as the photovoltaic effect and defines the performance of a photo-catalyst.

Photo-catalysis is used largely in commercial and environmental applications. Photo-catalytic research has grown in the late 1970s by several exciting publications concerning water splitting by using UV light [2]. Today research in photo-catalytic water splitting to produce hydrogen (H\textsubscript{2}) as an energy source has gained enormous interest for sustainable fuel production [3].

In the early 1980s the main research shifted to environmental applications where photo-catalytic reactions had an important role in purification processes as air cleaning and water purification [1]. Air cleaning became more and more urgent for health and environmental reasons and in many countries this urgency was supported by legislation. Photo-catalysis proved to be an attractive option for removing organic compounds, such as VOC’s from exhaust gas, which may cause undesirable effects on human health and environment [4]. Also the pollution of water formed a serious health problem that asked for solutions. Photo-catalytic purification of air and water shows promising results in nowadays research and gained industrial interest. It is an advanced oxidation/reduction process where low-energy ultraviolet light is coupled with a semiconductor as photo-catalyst. Organic substances are degraded into environmental harmless compounds, like water, carbon dioxide or non-toxic organics.

Also in industrial research the interests in photo-catalytic oxidation of hydrocarbons increased last decades. This interest origins mainly from the important role a photo-catalyst can play in the high selectivity towards a desired product. This high selectivity makes the use of catalysts activated by photons in hydrocarbon oxidation processes very attractive.

The research of the photo-catalytic oxidation of cyclohexane is of great interest to the caprolactam and adipic acid manufactures. The current industrial processes for cyclohexanone suffer from costly
separation processes for the reaction products to obtain pure cyclohexanone. Therefore, high selectivity to cyclohexanone is preferred. Du et al. [6] showed almost complete selectivity to cyclohexanone (above 95%) applying photo-catalytic oxidation of cyclohexane.

1.2. Cyclohexanone, an industrial important ketone.

Caprolactam and adipic acid are the main chemicals used for the production of most nylon, caprolactam for nylon-6 and adipic acid for nylon-6,6. The industrial and economic relevance of nylon-6 and nylon-6,6 is illustrated by the yearly turnover of more than € 10 Billion. Main use is in fiber applications (Table 1). These two chemicals can be formed from cyclohexanone and therefore the production of cyclohexanone is an important (between-) process for the nylon industry.

Table 1: Commercial relevance of Caprolactam [7] and Adipic Acid [8]. Key Figures for global markets 2007.

<table>
<thead>
<tr>
<th></th>
<th>Caprolactam</th>
<th>Adipic Acid</th>
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<tbody>
<tr>
<td>Turnover, € Bln</td>
<td>8</td>
<td>5,2</td>
</tr>
<tr>
<td>Volume, Million mt</td>
<td>4,0</td>
<td>2,8</td>
</tr>
<tr>
<td>Average Price, €/kg</td>
<td>2,00</td>
<td>1,85</td>
</tr>
<tr>
<td>Annual Grow Rate, %</td>
<td>2,8</td>
<td>3</td>
</tr>
<tr>
<td>Primary Applications</td>
<td>Nylon-6 textiles, resin, film, filament</td>
<td>Nylon-6,6 textiles, resin, lubricants, food additives</td>
</tr>
<tr>
<td>Primary Manufacturers</td>
<td>BASF (D)</td>
<td>Koch (USA)</td>
</tr>
<tr>
<td></td>
<td>DSM (NL)</td>
<td>Rhodia (FR)</td>
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<td></td>
<td>Honeywell (USA)</td>
<td>Solutia (USA)</td>
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<td></td>
<td>China Petr.Devpmt (China)</td>
<td>BASF (D)</td>
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<td></td>
<td>Ube Industries (J)</td>
<td>Liaoyang</td>
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<td></td>
<td>Sumitomo Chemical (J)</td>
<td>Petrochemical.(China)</td>
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<td></td>
<td>Bayer (D)</td>
<td>Asahi Chemical (J)</td>
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<td>Radici (I)</td>
</tr>
</tbody>
</table>

For caprolactam, cyclohexanone is the most common organic precursor, while for adipic acid production besides cyclohexanone also cylohexanol is used as a chemical intermediate.

1.2.1. Caprolactam production.

Commercial processes produce caprolactam via several steps of reactions where cyclohexanone is the starting material [9]. Honeywell (formerly Allied Signal), for example, is using acidic hydroxylamine sulfate for the production of cyclohexanone oxime [10, 11].
To convert cyclohexanone oxime to caprolactam, the so-called Beckmann rearrangement is applied involving a ring opening of the cyclohexyl ring by using oleum or sulfuric acid. Further reaction with ammonia leads to caprolactam.

As mentioned, for the production of the synthetic fiber nylon-6,6 adipic acid is an important chemical intermediate. Adipic acid can be produced by nitric acid oxidation of cyclohexanone, cyclohexanol or KA-oil (Ketone-Alcohol; a mixture of these two compounds). The reaction to adipic acid can follow several paths [9]. All these reactions start from cyclohexanone and via intermediate products it finally forms adipic acid.

The cyclohexanol must first be converted to cyclohexanone before it can react to adipic acid. It is preferable to start directly from cyclohexanone in order to prevent an extra step. In conclusion, cyclohexanone is required both for the production of adipic acid as well as for the production of caprolactam.

1.2.2. Cyclohexanone production.

Industry is applying several processes to produce cyclohexanone. Hydrogenation of phenol and (catalytic) air-oxidation of cyclohexane are the most common processes to produce cyclohexanone. In the air-oxidation cyclohexane is first converted to cyclohexyl hydroperoxide as a intermediate product, which reacts to either cyclohexanone and cyclohexanol. However, cyclohexane oxidation leads to low conversions (<10%) and the product is a mixture of cyclohexanone and cyclohexanol. To obtain pure cyclohexanone, cyclohexanol has to be converted to
cyclohexanone by further oxidation or the mixture has to be separated by distillation or other separation technologies.

\[
\text{cyclohexane} + \text{O}_2 \rightarrow \text{cyclohexanol} \rightarrow \text{cyclohexanone} + \text{cyclohexanol}
\]

Besides the low conversion, the production of cyclohexanol dominates the other reactions, which leads to high alcohol/ketone ratio. This ratio depends on the type of catalyst. A cobalt catalyst will lead to a ratio of 3.5 where a chromium catalyst leads to a lower ratio [9]. Other products that are formed in small amounts are carboxylic acids, esters, aldehydes and other oxygenated compounds.

Consequently, the low conversion in combination with the high ratio cyclohexanol/cyclohexanone is costly and energy consuming. Therefore process conditions leading to high cyclohexanone to cyclohexanol ratio are required for further industrial and economic optimisation.

1.3. Scope of the MSc graduation project.
Photocatalytic oxidation of cyclohexane is an alternative option for the production of cyclohexanone giving high selectivity to cyclohexanone [6]. However, the low reaction rate of the oxidation of cyclohexane, related to catalyst and reactor design, and the deactivation of TiO$_2$ catalyst cause large disadvantages to interest the chemical industry for commercialising this photo-catalytic reaction. These two problems have to be improved significantly before this photo-catalytic process can compete with the conventional processes for the production of cyclohexanone.

Improvement can be achieved by catalyst or reactor design, but this study will focus on the catalyst design. Photocatalytic oxidation processes are much studied. From enormous amount of publications concerning photocatalytic oxidation, only a few discusses the photo-oxidation of cyclohexane and even fewer this reaction with TiO$_2$ catalyst, as seen in Figure 1.

Studies on gas-phase oxidation [12-14] showed that dispersing gold on TiO$_2$ catalyst surface gave high activities. Also, the use of gold catalysts in liquid phase oxidation received more attention recently, such as the oxidation of alcohols [15-17].
This leads to the scope of this MSc graduation project. Main focus is to increase the reaction rate of the photocatalytic oxidation of cyclohexane by improving the catalyst performance. The use of these Au/TiO₂ catalysts for cyclohexane photo oxidation has not been reported earlier.

Special focus in this project is on how Au/TiO₂ influences:
1. the photocatalytic activity of various oxidation reactions (effect of better charge separation)
2. the deactivation behaviour of the catalyst and
3. the oxidation reaction of organic gases in the visible light range

The project consists of three parts to study the influence of gold deposition on TiO₂ surface.

- Preparation of photocatalysts.
  The preparation method of dispersed gold on TiO₂ will have influences on the performances of the catalyst. The Au particle size, the method for reduction of gold and the TiO₂ support are some examples which might influence the catalytic activity.

- Characterization of catalysts.
  Analysis techniques will be used to examine these catalyst properties and will lead to a relation between the activity/selectivity and the characteristics of the prepared catalysts. The characterization of the catalysts is planned to be done for pore texture by nitrogen physisorption, for active sites by ammonia-TPD, for gold particle size by transmission electron microscopy (TEM), structure phase by X-ray diffraction (XRD), etc.
• Photo-catalytic oxidation reaction.

The most important part of the project will be the testing of the prepared catalysts in photo-catalytic processes, in particular, the photo-catalytic oxidation of cyclohexane. Hereby, the initial reaction rate, deactivation of the catalyst and the selectivity to cyclohexanone are the most important parameters to follow.

The prepared catalysts will also be tested for other photo reactions and in other reaction conditions, to check these parameters on the catalytic performance. This will be done by the decomposition of methylene-blue, which will indicate the degradation activity of the catalysts which could be used for purification applications. Furthermore, one catalyst is used for gasphase photo-oxidation of propane in visible light range. In the same experimental set-up, direct photo-catalytic oxidation of propylene with water is tried out for epoxidation.
2. THEORETICAL CONSIDERATIONS

2.1. Semiconductors

2.1.1. Band gap and donors/acceptors

Metals, semiconductors and insulators are built up of a band structure [18]. Figure 2 shows three configurations which are distinguished by the occupancy of the energy bands. The highest energy band of metals is partially filled with electrons, however there is no barrier for excitation of electrons to higher energy levels. Semiconductors and insulators contain a band gap, which is the gap between the top of the valence band and the bottom of the conduction band. The energy difference between these two energy bands is called the band gap energy, also $E_g$. Semiconductors have narrow band gaps (<4.0 eV), whereas insulators have very large band gaps (>4.0 eV).

![Figure 2: Bandgap in (a) metal, (b) semiconductor, (c) Insulator [18].](image)

Photocatalytic reactions are the results of the interaction of photons with a semiconductor (Figure 3). When the arriving light has an energy level equal or greater than the semiconductor band gap, radiation is absorbed and electrons (negative charge carriers) are jumping from the valence band to the conduction band. The unoccupied state that is left behind in the valence band is called a hole, which is a positive charge carrier. These generated carriers are called electron-hole pairs. After a random motion through the lattice, the electron in the conduction band encounters a hole and undergoes recombination. However, these charge carriers can also migrate to the catalyst surface where they can participate in oxidation and reduction reactions. The electron can be donated to an electron acceptor such as oxygen, leading to a superoxide anion.
Semiconductors can be divided in intrinsic and extrinsic semiconductors. Intrinsic semiconductors are pure semiconductors and do not contain impurities or defects. The activation of an electron from the valence band to the conduction band gives a free electron in the conduction band and a free hole in the valence band. There are no energy levels present within the band gap. Consequently, activation of electrons by light can occur only when light has an energy level exceeding the band gap energy. However, mostly the energy of light in the visible range appears to be insufficient to activate electrons; the bandgap is too high. Dopants (impurities) might introduce another band between the valence and conduction band resulting in a lower bandgap for activation of electrons. With these dopants, visible light might activate electrons at lower energy levels. Semiconductors with these dopants or impurities are called extrinsic semiconductors. Extrinsic semiconductors contain impurities which are brought into the lattice during preparation of the semiconductor, e.g. by mixing an Au solution during the sol/gel preparation of TiO$_2$ [19]. This process is called doping.

Dopants provide free carriers by accepting or donating an electron. Donors donate electrons to the conduction band and acceptors supply holes in the valence band.

Donors are impurities (e.g. phosphorus atoms) which have more electrons than its host material (e.g. germanium). Most electrons of the impurity are located in the valence band, but the remaining electron(s) has no valence band to occupy. Therefore the electrons are situated in the so-called donor band, which is higher than the valence band. Due to the attraction of the electron(s) by the high positive charged impurity atom (e.g. phosphorus is +5), this band is situated just below the conduction band minimum (Figure 4a). Such material is called an n-type semiconductor (n corresponds with negative).
When the dopant (e.g. aluminium atoms) has fewer electrons than its host material (e.g. germanium), it is called an acceptor and can trap electrons. The acceptor band (Figure 4b) is situated just above the valence band maximum and can withdraw electrons from this filled band. This will leave holes, which will allow the remaining electrons to move creating mobile holes. This semiconductor is identified as a p-type semiconductor (p stands for positive).

So, doping of impurities into the lattice of a semiconductor makes it possible for electrons with less energy to jump to a higher band. This makes the semiconductor more sensitive for visible light.

2.1.2. TiO$_2$ structures

Semiconductors as ZnO, ZnS, WO$_3$, CdS, etc. are widely used photo-catalysts [20], but the most used photo-catalyst is titanium dioxide (TiO$_2$). It is chemical and biological inert, photo-stable and has low-toxicity. Furthermore, TiO$_2$ has great availability and therefore is relatively cheap.

Titanium dioxide can be divided in three major crystallized structures; rutile, anatase and brookite. Rutile and anatase plays the most important role in applications of TiO$_2$. The structures are both given in Figure 5.

![Figure 5: Crystal structures of TiO$_2$ [20].](image)
Anatase is thermodynamically unstable and converts to rutile after heating to high temperatures. However, anatase is the structure with the highest photocatalytic activity and has a band gap energy of 3.2 eV and is excited with UV-light. Rutile has a band gap of 3.0 eV and is considered less photocatalytic active, although it is more widely used than anatase (e.g. purification processes). Especially as white pigments rutile is applied extensively, due to its higher light diffraction/scattering.

2.2. Proposed mechanism for photo oxidation

A proposed mechanism of photocatalytic oxidation is described by Du et al. [6] and is shown and explained below for the oxidation of cyclohexane:

![Reaction scheme proposed for the photo-oxidation of cyclohexane to cyclohexanone [6]](image)

The first step implies a reaction between a photon-activated hydroxyl group and the adsorbed cyclohexane, producing a cyclohexyl radical and water. The created Ti(III) center activates oxygen to a surface O$_2^-$ anion. This will lead to recombination of the cyclohexyl radical and the O$_2^-$ anion creating a peroxide intermediate. Finally the peroxide intermediate decomposes into cyclohexanone molecule and a hydroxyl group on the catalyst surface.

However, it is known that the cyclohexyl hydroperoxide intermediate can also be catalytically decomposed into an alcohol instead of the ketone. A photon-activated hydroxyl group can react with the surface cyclohexyl radical resulting in surface adsorbed cyclohexanol. Degradation of the surface cyclohexanol with superoxide anions may lead to carboxylates, resulting in deactivation of the catalyst and to further oxidation towards carbon dioxide (CO$_2$).
2.3. Catalyst selection and experimental set-up for catalyst preparation.

The selection of catalysts and the experimental set-up for catalyst preparation has been made after evaluation of earlier studies on the photo catalytic activity of TiO$_2$.

2.3.1. Effect of type of TiO$_2$ support on photo catalytic activity.

As discussed before there are three types of crystal structures in TiO$_2$: rutile, anatase and brookite. The fact that the band gap value of rutile is less than of anatase, rutile TiO$_2$ can absorb light closer to the visible range, and therefore it is more widely used in environmental and commercial applications than anatase (e.g. purification processes). However, in reality, anatase exhibits higher photo-catalytic activity, due to the difference in the position of the conduction band, resulting in a stronger reducing power of anatase. It is known that commercial available TiO$_2$ supports have different catalyst composition and catalyst texture, which results in different photo-catalytic activity. Physical properties of some commercial TiO$_2$ are shown in Table 2.

<table>
<thead>
<tr>
<th>Table 2: Some characteristics of commercially available TiO$_2$ catalysts (Supplier data)</th>
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<tbody>
<tr>
<td><strong>Anastase/Rutile</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Hombicat (UV 100)</td>
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<td>Degussa P25</td>
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</table>

In spite of the considerably higher anatase percentage and specific surface area of Hombicat UV 100, the photo-catalytic activity reported in literature is not always higher when compared to other TiO$_2$ catalysts. For example, Mehrvar et al. [21] reports for the degradation of alkyl benzene sulfonate a higher photo-catalytic activity for Degussa P25 at lower loading values. Similar behaviour was reported by Du for Hombicat and Degussa P25 for the decomposition of methylene blue, but he also found the opposite in the photo-oxidation of cyclohexane to cyclohexanone [22].

Besides commercially available TiO$_2$ catalysts, also specially prepared TiO$_2$ catalysts with tailored properties show promising results in activity, e.g. for CO oxidation with supercritical prepared TiO$_2$ [23]. See also Appendix 2. In this MSc-project only commercially available TiO$_2$ will be studied, due to lack of availability of specific equipment e.g. SAS apparatus to produce super critical TiO$_2$ and due to the limited time available within this project. However, due to the large variances in photo-catalytic activity in commercial available catalysts, it might be worthwhile to optimize the TiO$_2$ catalyst properties by tailoring certain properties.

In conclusion, the selection of TiO$_2$ support might depend to a large extent on the type of oxidation reaction. In spite of the high photocatalytic activity of Hombicat in the oxidation of cyclohexane to cyclohexanone, other catalyst supports might work better for Methylene blue decomposition (larger molecular size, aqueous medium, other degradation products). Furthermore, also the effect of Au deposition and the reduction method from Au$^{3+}$ to metal Au might be different for each catalyst.
support. Therefore, several commercially available TiO₂ supports are proposed to be studied. Moreover, this gives an opportunity to compare our results of catalyst preparation with earlier studies.

2.3.2. Effect of catalyst loading and reactor type on photo catalytic activity.

The photo-catalytic activity and selectivity of TiO₂ depends on catalyst loading and reactor type. Du et al. [6] found that the reactor material and applied amount of catalyst affects the selectivity of the oxidation of cyclohexane to a great extend. For photolytic oxidation of cyclohexane, without any catalyst, the selectivity to cyclohexanone is <15%, while the selectivity increases enormously to over 95% when a photocatalyst is applied as depicted in Figure 7.

![Figure 7: A: No catalyst, Quartz reactor. B: TiO₂ catalyst, Quartz reactor. C: TiO₂ catalyst, Pyrex reactor. D: No catalyst, Pyrex reactor.](image)

The influences of the reactor materials and catalyst loading are discussed in detail in Appendix 3. Highest selectivity to cyclohexanone is achieved with a Pyrex reactor filled with the photocatalyst. Not shown, but discussed in Appendix 3 is the existence of a maximum in catalyst loading at around 1g/L. Higher loading will lead to induction of the catalytic surface reaction, but also blocks the light that illuminates the reaction mixture.

In conclusion: Favourable conditions are 1. reactor of Pyrex glass and 2. TiO₂ catalyst loading of the reactor at around 1g/L.

2.3.3. Effect of metals on photo catalytic activity.

The low conversion of cyclohexane and the deactivation of TiO₂ catalyst cause large disadvantages to interest the chemical industry photo-catalytic oxidation of cyclohexane. Photocatalytic catalysis can be improved by the use of metals [1]. Two methods for the use of metals are metal doping and metal coating (deposition). Metal doping is shortly discussed in Appendix 4, however the photo-physical mechanism of doped semiconductors is not always understood and the effect of metal ion dopants on
the photocatalytic activity is a complex problem. Therefore, deposition of metals on the catalyst surface seems to be a practical way to stimulate the photo-oxidation process at the catalyst surface. Below, deposition of metals is explained in more detail.

Deposition of noble metals onto the surface of TiO\textsubscript{2} will create a Schottky barrier at each metal-semiconductor region [24]. This reduces the electron-hole recombination and creates an efficient charge separation. This charge separation enhances photocatalytic reactions by changing the amount of electrons transferred to oxygen molecules. Deposition of noble metals (like Au) on the photocatalytic surface stimulates and consequently increases the electron transfer rate of oxygen and thereby enhancing the reaction rate in oxidation processes (Figure 8). Gold supported catalysts are reported in application as gas-phase oxidation, selective oxidation of alkenes and degradation of organic compounds in purification processes. The catalytic properties are strongly dependent on the gold particle size and type of support.

Figure 8: Schematic representation of electron capture by noble metal (NM) deposit at a semiconductor surface [24].

The loading of the deposit also plays an important role on the photocatalytic activity. There is an optimal loading value and exceeding this value affects the photocatalytic activity negatively. A high number of metal particles on the surface of the semiconductor catalyst can block the photons reaching the TiO\textsubscript{2} surface. This reduces the amount of photogenerated hole-electron. Deposition of metals mostly increases the photocatalytic activity. However, for some reactions the deposition of metals can also decrease the photocatalytic activity. For example, the addition of Pd, Pt and Ag reduces the efficiency for degradation of chlorinated hydrocarbons, but leads to an increase of alcohol photodegradation [1]. Suggested reasons are the development of degradation products which could deactivate the catalyst.

Nijhuis & Zwijnenburg (R&CE, TUDelft [12,13]), Dimitratos [25] and Harata [26] all developed and studied deposition of gold on TiO\textsubscript{2} support for different catalytic applications. From these studies an optimal choice could be made for the catalyst preparation.
2.3.3.1. Au/TiO₂ as catalyst for new propylene oxide process.
Nijhuis [12] and Zwijnenburg [13] did a lot of research for a new propylene oxide process using dispersed gold on TiO₂ catalyst. They prepared Au/TiO₂ catalysts using Degussa P25 TiO₂ (70% anatase, 30% rutile) as TiO₂ supports and gold(III)chloride as gold precursor. Well dispersed gold particles of 3-10 nm were obtained on the Degussa P25 TiO₂ support. The success of this research has lead to the decision of the BASF-DOW joint venture to build a new propylene oxide production plant in Antwerp which is based on this technology, which is expected to in operation in 2008 [27].

The catalyst preparation consists of two parts; deposition-precipitation and the reduction of gold. Precipitation is the formation of solids, in this case gold, from a solution which will deposit onto the TiO₂ support. The reduction method is necessary to reduce Au(III) species to obtain the metallic Au particles on TiO₂ surface. Calcination is used as reduction method (Figure 9).

Calcination is the thermal treatment to obtain the phase transition to metallic gold (reduction). The TiO₂ surface contains Au(OH)₃ species after the deposition-precipitation of the gold precursor. During calcination the gold is reduced and water is removed by dehydroxylation. The particle formation depends on the calcination temperature. Most gold is present in a metallic form after treatment above 573 K.

2.3.3.2. Au/TiO₂ as catalyst for oxidation of glycerol.
Dimitratos et al. [25] discuss the effects of preparation method and reduction methods on the Au/TiO₂ catalysts for the oxidation of glycerol in water as a model reaction. The preparation methods are immobilisation and deposition-precipitation (DP). The two reduction (activation) methods studied are calcination and chemical reduction with NaBH₄. Chemical reduction is a process where chemically the positive valence state of gold is lowered to metallic gold.
The oxidation states are determined by X-ray photo-electron spectroscopy (XPS), although the results of Table 3 have to be interpreted carefully, because the photon beam of the XPS might reduce Au(III) to Au(0) too. The particle sizes are measured by high-resolution TEM (HRTEM). The catalytic activity (TOF) is calculated after 0.5h of reaction. The first four samples are prepared by deposition-precipitation (DP), while sample 5 and 6 are obtained by immobilization and sample 7 is a commercially available Au/TiO$_2$ catalyst supplied by World Gold Council (synthesised by deposition-precipitation).

Sample 1, without reduction, has the smallest Au particle size (1-2 nm) with no catalytic activity at all. The XPS data show two oxidation states for gold, Au(0) at 83.9eV and Au(III) at 85.1eV, corresponding to a presence of respectively 48% and 52%. However, Mossbauer analysis on the same sample reveals only Au(III) species were present. It is believed that the photon beam of XPS reduces some Au(III) species to Au(0) species.

Different methods of reduction lead to different results in particle characteristics. Firstly, chemical reduction with NaBH$_4$ (sample 3) leads to larger particle sizes (2-5 nm) than without reduction. Calcination (sample 2) results in particles of around 5 nm. Secondly, the XPS data reveal that calcined catalysts have two oxidation states, namely Au(0) and Au(δ+), while the catalyst that is reduced with NaBH$_4$ has only Au(0) as oxidation state.

Samples 5-7 have all metallic gold (Au(0)) as oxidation state only. The commercially Au/TiO$_2$ (sample 7) is used as a reference catalyst, for samples 5 and 6, to confirm the influence of gold particle size on the catalytic activity. Sample 5 gives smaller particle size and higher catalytic activity, while for sample 6 this is the other way around. Thus smaller particle size influence the catalytic activity positively, but under 2 nm catalytic activity is reduced to nil.

The combination of DP and reduction with NaBH$_4$ gives the highest catalytic activity (TOF). DP with calcination gives much lower catalytic activity and DP with the combination of chemical reduction/calcination (sample 4) gives even worse results.
2.3.3.3. Au/TiO$_2$ as catalyst for reaction of propylene with O$_2$ and H$_2$.

Haruta [26] also studied the size dependency of gold particles in photo-catalysis. In the reaction of propylene with O$_2$ and H$_2$, the smallest particle size is 2 nm to be catalytically active (see Figure 10). The catalyst is inactive, when the particle size is below 2 nm. This result is in line with the results of Dimitratos [25] as discussed above.

![Figure 10: Product yields for reaction of propylene with O$_2$ and H$_2$ over Au/TiO$_2$ catalysts as a function of the mean diameter of Au particles [26].](image)

Summarized:

- No reduction will give mostly Au(III) species on the TiO$_2$ surface.
- Calcination results in growth of the Au particles.
- Small Au particles have higher catalytic activity than large particles.
- Calcination results in two oxidation states, where Au(0) is the major component and Au(III)/Au($\delta^+$) the minor species. By chemical reduction only gold in metallic phase (Au(0)) is obtained. Metallic gold (Au(0)) is the active phase.
- For glycerol oxidation it was found that deposition-precipitation followed by reduction with NaBH$_4$ resulted in the most active catalyst.

In conclusion, favourable conditions are:

- As much as possible metallic gold and as less as possible Au(III) and A ($\delta^+$).
- Reduction of NaBH$_4$ leads to highest percentage metallic gold and to highest catalyst activity.
- Particle sizes not below 2 nm.
2.4. Experimental approach.

a. Selection of catalyst.
Four commercially available TiO$_2$ will be used in this study. In order to connect to the experience at R&CE in preparing Au/TiO$_2$ photo catalysts, the method which has been applied by Nijhuis [12] and Zwijnenburg [13] will be used as starting point. Deposition-precipitation is followed by calcination of the catalysts. They used Degussa P25 TiO$_2$ as support. Due to the favourable results in many photo catalytic studies and its superior surface area and high anatase content, Hombicat TiO$_2$ is selected as the support to be studied in most detail. For both TiO$_2$ supports both the effects of Au loading and of reduction method (calcinations and chemical reduction by NaBH$_4$) on active sites density and surface area will be studied. The other two supports of Merck and Aldrich will be studied on Au loading (followed by chemical reduction) only.

b. Characterization.
The prepared catalysts will be characterized by nitrogen physisorption, ammonia-TPD, transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), UV-VIS, etc. These analyses will determine properties as surface area, pore distribution, amount of surface hydroxyl groups, Au particle size, etc. The examined catalyst properties will indicate the influences of the different preparation methods on these properties. Furthermore, the relation of these catalyst properties and the catalysts activity can be studied in several photocatalytic processes.

c. Photo oxidation reactions.
The fresh Au/TiO$_2$ catalysts will be tested on their photo-catalytic activity in several processes, differing in liquid or gas phase and in organic or aqueous environment

c.1. Cyclohexane oxidation to cyclohexanone (organic/liquid)
The main focus is the catalytic activity in the liquid phase photo-oxidation of cyclohexane to cyclohexanone. This will be done in an immersion-well reactor, which was also used in the research of Du et al [6]. Also the selectivity towards the main product is high importance and will be studied. Light intensity tests of the UV-lamp are necessary to compare, in the future, this reactor configuration with other reactor set-ups.

c.2. Water purification (aqueous/liquid)
The prepared catalysts for cyclohexane photo-oxidation will also be applied in other photocatalytic processes. The photocatalytic activity of the catalysts for purification processes can be tested by the degradation of methylene blue.

c.3. Propane/propylene oxidation (organic/gas)
Some preliminary experiments are planned to study the photo-catalytic oxidation of propane with molecular oxygen at several wavelengths including visible light. Furthermore, some first shots are planned to get information if the direct oxidation of propylene in the presence of water leads to epoxy formation These gas phase reactions are foreseen using the in-situ FTIR equipment at the University of Leiden.
3. EXPERIMENTAL


All catalyst precursors are prepared by deposition-precipitation. The catalyst precursor is activated by calcination and chemical reduction with NaBH₄. The chemicals and compounds that were used for the preparation of the catalysts are listed in Table 1, Appendix 5.

The target was to get around 10 gram catalyst of each type. The support (TiO₂) was dispersed in distilled water (10 gram TiO₂ in 100ml water) to which ammonia was added to raise pH to a value between 9 and 10. The suspension was vigorous stirred to get a uniform pH and support concentration throughout the solution. All preparations were performed at room temperature.

The required amount of AuCl₃ was dissolved and stirred in 300 ml distilled water. Due to reaction with air and light, gold flakes were formed and these were filtrated from the AuCl₃ solution. Over a period of two hours this eluent was added dropwise to the suspension, meanwhile the pH was kept between 9 and 10 manually. The mixture was stirred for another half an hour after which it was filtrated and washed two times with distilled water.

Before the catalyst precursor is activated by calcination, the precursor was dried overnight in an oven of 80°C. Calcinations were executed for 4 hours at 400°C, with heating ramp of 5°C/min. For chemical reduction, the catalyst precursor was dissolved again in 100 ml distilled water. A solution of NaBH₄ (0.1M) was prepared and added in the required amount (NaBH₄/Au = 5 mol/mol) under vigorous stirring. The mixture was stirred for another half an hour after which it was filtrated and washed again two times with distilled water. The obtained catalysts were dried in an oven at 120°C. Furthermore, the non-gold TiO₂ catalysts were dried overnight in an oven at 120°C too, to evaporate water and other volatile components. All obtained gold catalysts have a pinkish purple colour.

3.2. Photo oxidation of cyclohexane to cyclohexanone.

3.2.1. Light intensity tests.

Before the experiments of the photo-oxidation of cyclohexane were performed, the lamp was examined on its intensity. The used lamp is a medium pressure mercury lamp of 450W (supplied by ACE Glass) Light intensity of the lamp was determined by an AVS - MC2000-3 (Avantes) with a light detector FC-UV200-4.

Two tests were performed at different locations of the reactor.

The first intensity test is done by measuring the light intensity directly at the surface of the immersion-well. This test determines the photon flux of the lamp at the exit of the immersion-well at the inside of the reaction medium which is in contact with the immersion-well. The second test is done on the outside wall of the reactor. These data determine the photon flux at the outside of the reaction medium, which is in contact with the outer wall of the reactor. The reactor contains only cyclohexane and no catalyst particles. In Appendix 6 the experimental set-ups of both tests are given. The light intensity is measured at various positions along the vertical axis of the immersion-well as well as the reactor. For each position the light intensity is measured and is used for calculating the photon flux at
that position. An average photon flux is used in calculating the conversion as function of photonic efficiency. This photon flux is the amount of photons that are available for reaction. The photonic efficiency ($\xi$) is described as product molecules formed per Einstein of photons.

The results of the light intensity test is shown in Appendix 7. The photon flux distribution along the lamp corresponds with a normal distribution; at both ends of the lamp the light intensity is low, while in the middle a high intensity is measured. The photon flux measurement on the outside of the reactor shows a smoother normal distribution than the measurement direct on the inner-well. This is due to the scattering of photons during the path from the lamp to the sensor. Furthermore the average photon flux at the outside of the reactor ($3.01 \cdot 10^{-4}$ Einstein/s/m$^2$) is lower than at the inner-well ($6.17 \cdot 10^{-4}$ Einstein/s/m$^2$), due to a quadratic decrease of intensity by distance and some light absorption from the reactor.

3.2.2. Reactor set-up.

The photocatalytic partial oxidation of cyclohexane is investigated using a photo-catalytic slurry reactor (Aceglass, type 7861-255, dimensions in Appendix 8). The set-up is presented in Figure 11, while the used chemicals are given in Table 2, Appendix 5.

Catalysts are suspended in the solution by mechanical stirring and bubbling of air into the reactor. A Pyrex glass cooling well is immersed into the reactor vessel. This immersion-well is made of Pyrex glass to cut off light with wavelength less than 300 nm. A medium pressure mercury lamp of 450 W inside the cooling well illuminates the reactor. The whole system is operated under conditions of atmospheric pressure and a temperature of 40°C.

Air is bubbled into the reactor, which comes from a central gas pipeline (6 bar). In order to remove the fraction of water from the gas line, the gas will first pass a drying bottle filled with silica particles before bubbled into the reactor.

The reactor is brought to the reaction temperature by a thermostat. The temperature inside the reactor is used to control the water bath. Consequently, overheating of the system is prevented. The waterbath itself has a safety shut-down system, of which the maximum temperature for safe operation is set at 45°C. Due to the low conversions, the produced heat is negligible and the reaction medium will never exceed 45°C. The system pressure is kept at 1 bar, by opening the gas outlet to the surrounding environment. In order to remove volatile organic compounds in the outlet gas, it is passed through a reflux cooler and a water trap consecutively before venting. During the reaction, liquid samples are taken manually from the sampling line, which passes through the interior of the reflux cooler. Gas samples are taken manually from gas outlet line by opening a valve. The liquid sample analysis is performed off-line by GC-FID. The gas sample analysis is done by GC-TCD.
3.2.3. Experimental procedure.

The photocatalytic reactor is filled with cyclohexane (600 ml), hexadecane (1 g) and catalyst (0.6 g). Hexadecane is used as internal standard in the GC analysis. The slurry is ultrasonicated to disperse the particles. This is done by positioning an ultrasonic bath under the filled reactor for ½ h, without the UV-lamp, because vibrations of the ultrasonic bath might cause failure of the UV-lamp. Subsequently, the cooling water for the thermostat and the reflux cooler are switched on. The lamp is installed in the reactor and the slurry is stirred and brought to the reaction temperature (40°C) by circulating the water from the thermostat through the inner well. The lamp is still switched off. The whole reactor is covered by aluminium foil to prevent lab personnel being exposed to UV irradiation.

When all conditions are set, the air inlet (300ml/min) is switch on. The first 30 minutes the reactor is operated without UV-light. The reaction starts when the power supply of the mercury lamp is switched on. Liquid and gas samples are taken at certain time intervals at the sample points (see Figure).

The samples are analysed off-line by means of gas chromatography. The gas samples are determined manually by a gas chromatograph CHROMOPACK CP9001. The liquid samples are analysed by a gas chromatograph CHROMOPACK CP9001 with a CPwax52CB column. The liquid samples are injected with a liquid sampler CP9050.
3.3. Photo oxidation of Methylene-Blue.

Methylene blue decomposition is carried out as model compound to examine photocatalytic activities in water purification of the prepared catalysts. The oxidative decomposition is irreversible and the colour turns from blue to colourless (Figure 12, [28]).

![Figure 12: Oxidative, irreversible decomposition of methylene blue](image)

3.3.1. Experimental set-up.

Several beaker glasses, which are filled with methylene blue (MB) aqueous solution, containing catalyst particles are placed on a multipoint magnetic stirrer (Figure 13). UV light (360nm) is produced by 8 (18W) black lights, which are fixed at the ceiling of the UV-box. The black lights obtains a narrow range of wavelength around 360nm. The temperature and humidity in the box are measured by a thermometer and a hygrometer respectively; a detailed set-up is shown in Appendix 9. An electric fan and a heating/cooling tube regulate the temperature in the box during the experiment. The cooling/heating water is circulating through a thermostat and the cooling/heating tube. A black curtain will cover the opening of the box, to prevent illumination of the beaker glass from outside. Samples are taken by syringes through the black curtain. These samples are analysed off-line by absorbance spectra.

![Figure 13: Experimental set-up for photo-oxidation of methylene blue](image)

3.3.2. Experimental procedure.

The used chemicals are listed in Table 3, Appendix 5. The methylene blue aqueous solution (0.03mM) is prepared in an UV-protected 1L flask. Beaker glasses of 250ml are filled with 100ml of the 0.03mM MB solution and 50mg catalyst. The beaker glasses are placed on the multipoint stirrer and are
covered with cover glasses to prevent as much evaporation as possible. The temperature is controlled at 30°C (± 3°C) by the cooling/heating tube and the electric fan in the box. The experiment starts after the UV black lights are switched on and a sample is taken (t=0). Samples are taken at certain time intervals by syringes. The samples are filtered through 0.45µm Millipore membrane filters (PALL, Acrodisc syringe filters) to remove the catalyst particles before analysis; this prevents further reaction. The samples are analysed in cuvets by an UV-VIS spectrophotometer (Avantes). Calibration based on Beer-Lambert law is used to quantify the dye concentration (Appendix 10).

3.4. Propane/Propylene photo-oxidation.

The normal oxidation of propylene over gold catalysts at high temperatures is leading to a higher selectivity to propylene oxide [13]. Only the obtained Au/P25 catalysts obtained by calcination are tested on their photocatalytic activity of propylene oxidation, because this was the exact same catalyst that was used by Zwijnenburg and Nijhuis.

3.4.1. Experimental set-up.

The photo oxidation reactions of propane and propylene are done with Au/TiO₂ (Degussa P25) as photo catalyst. The reaction is executed with oxygen or water at different wavelengths. All these experiments are performed in the in-situ IR equipment at the University of Leiden using Fourier Transform Infrared (FTIR) to determine conversion. The light source is a 500 W capillary Hg lamp (Philips SP500). Certain wavelengths are isolated by using a monochromator and glass filters, giving a bandwidth of approximately 15 nm. The wavelength intensity is measured with a thermopile power meter (Scientech 360001). Catalyst wafers are prepared, at which the gas reactants are absorbed to the surface. The wafers are pressed at a 3 tons/cm² automatic press (SPECTA). The wafer is placed in a copper sample holder, which is mounted in the optical tail of a stainless steel high-vacuum system. The tail is positioned in the sample area of a FTIR spectrophotometer (Bio-Rad 176C). By using CaF₂ windows and protecting the detector with a germanium plate, FTIR spectra can be obtained during UV light irradiation. At switching on the Hg-lamp the photo oxidation starts. The FTIR set-up is given in Figure 14.

![Figure 14: Schematic set-up of the FTIR equipment.](image)
3.4.2. Experimental procedure.

All catalyst wafers prepared are activated by heating under high vacuum to 500°C, and maintaining this temperature for 30min. After this activation cycle the temperature is cooled down again to room temperature. It is possible to make a certain gas mixtures of propane or propylene with water or oxygen in the sample chamber of the set-up. The reactants will adsorb onto the catalyst surface. The IR absorption spectra of each experiment are taken before, during and after reaction. These data provide information of the photo-catalytic performance of the catalyst in the oxidation process of propane and propylene.

Two experiments are performed, i.e.:

- Oxidation of propane with oxygen over Au/TiO₂ catalyst at 365nm, 435nm and 545 nm
- Oxidation of propylene with water over Au/TiO₂ catalyst at 365nm.

It has to be noticed that the lamp at different wavelengths have different light intensities, respectively 220, 90 and 66 mW/cm² for wavelengths of 365,435 and 545 nm.

The used chemicals can be found in Table 4, Appendix 5.
4. RESULTS AND DISCUSSION


4.1.1. Nitrogen physisorption and ammonia-TPD.
Determination of the porous properties and the surface acidity of the catalysts are done by volumetric N2 physisorption at 77K and temperature programmed desorption (TPD).
After pre-treatments of the samples to remove moisture and other volatile components, the nitrogen adsorption and desorption isotherms were recorded by a QuantaChrome Autosorb-6B at 77 K. The isotherms provide information on the surface area ($S_{BET}$), the pore volume, the pore size distribution and the micropore contribution (Appendix 11).
Temperature-programmed desorption of ammonia (NH3-TPD) between 373 K and 773 K (10 K/min) was carried out at a Micrometrics TPR/TPD 2900 apparatus equipped with a thermal conductivity detector (TCD). This provides information on the total amount of active sites and an indication of the acidity of the surface groups (Appendix 11).

4.1.1.1. Catalysts obtained by calcination.
For both Hombicat and Degussa P25 photocatalysts were prepared with and without dispersed gold particles by calcinations at 673K for 4 hours. In Table 4 the surface area and the acidic-OH group density of various catalysts are given, the TPD profile can be found in Appendix 11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au loading</th>
<th>TiO2</th>
<th>Acidic-OH (mmol/g)</th>
<th>$S_{BET}$ (m2/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>0 wt%</td>
<td>Hombicat</td>
<td>0.66</td>
<td>160</td>
</tr>
<tr>
<td>Au/TiO2</td>
<td>0.6 wt%</td>
<td>Hombicat</td>
<td>0.62</td>
<td>156</td>
</tr>
<tr>
<td>Au/TiO2</td>
<td>2.0 wt%</td>
<td>Hombicat</td>
<td>0.63</td>
<td>147</td>
</tr>
<tr>
<td>TiO2</td>
<td>0 wt%</td>
<td>Degussa P25</td>
<td>0.30</td>
<td>51</td>
</tr>
<tr>
<td>Au/TiO2</td>
<td>0.6 wt%</td>
<td>Degussa P25</td>
<td>0.27</td>
<td>49</td>
</tr>
</tbody>
</table>

The dispersion of gold is lowering the surface area a few percentage only. It is suggested that the gold particles are blocking the pores of the TiO2, which results in the decrease of the specific surface area of the catalyst. Also the amount of OH groups is decreasing by the addition of gold particles, due to blocking these groups on the TiO2 surface by the gold particles and due to the high calcinations temperature for 4 hours. A representation of these processes can be found in Figure 16.
Figure 16: Schematic representation of decrease of OH groups by gold deposition.

For Hombicat catalysts without any dispersed gold particles, Du [6] reported similar results. Moreover, these catalysts are calcined for 4 hours too, but at different temperatures. At higher calcinations temperatures both the OH density and the surface area are decreased strongly as shown in Table 5 and Figure 17.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>OH groups (mmol/g)</th>
<th>S_{BET} (m^2/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>393</td>
<td>0.92</td>
<td>337</td>
</tr>
<tr>
<td>673*</td>
<td>0.66</td>
<td>160</td>
</tr>
<tr>
<td>773</td>
<td>0.33</td>
<td>113</td>
</tr>
<tr>
<td>1073</td>
<td>0.07</td>
<td>18</td>
</tr>
<tr>
<td>1373</td>
<td>0.009</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 5 and Figure 17: Active sites and specific surface area for Hombicat catalysts calcined at different temperatures

The pre-treatment temperature will have a significant effect on the Hombicat composition and texture, which cause the decreasing profile.

Furthermore, the pore distribution (Appendix 12) of the samples indicates that the Hombicat based catalysts own more micropores (peak at 44Å) in contrast of the Degussa P25 catalysts which has macropores (peak at 526Å).

4.1.1.2. Catalysts by chemical reduction.

The pre-treatment temperature during calcinations will change the surface area and OH groups of the Hombicat catalyst tremendously, due to composition and texture change of Hombicat. By activating the gold on the TiO_{2} surface of the catalyst with NaBH_{4}, during the chemical reduction, this effect can be reduced. Table 6 presents the data of all catalyst produced by the deposition-precipitation method followed by chemical reduction with NaBH_{4} (obtained from the TPD profiles (Appendix 11)).
The high surface area and amount of OH groups are maintained almost totally during the chemical reduction for the Hombikat-based catalysts compared to calcination as activation method. This in contrast to the P25-based catalyst, where the surface area remains the same and the amount of OH groups decreases. Compared to the calcined Au/P25, the amount of OH groups decreased drastically. It is believed that NaBH4 during the chemical reduction are blocking the OH groups more than at the other supports. The other two supports, Merck and Aldrich, are showing to have really low surface area and amount of OH groups in contrast to the first two supports, already before chemical reduction. The pore distribution (Appendix 12) shows the same results as in the calcination method for Hombikat and Degussa P25. The distribution of Merck and Aldrich TiO₂ supports shows these catalysts have macro pores only.

### 4.1.2. TEM.

The technological principles of a transmission electron microscope (TEM) are similar as an optical microscope. The difference is the use of a beam of electrons instead of a beam of light. This makes the resolution much higher due to the shorter wavelength of the electrons. On a TEM image heavy atoms are observed as dark spots, caused by stronger absorption and scattering of the electrons. TEM was performed using a Philips CM30UT electron microscope with a FEG (field emission gun) as the source of electrons operated at 300 kV. Samples were mounted on Quantifoil® microgrid carbon polymer supported on a copper grid by dripping sample suspension on the grid.

#### 4.1.2.1. Catalysts obtained by calcinations.

The three TEM images below represent the catalysts prepared by the calcination method. These three catalysts are prepared by deposition-precipitation of Au(OH)₃ (with AuCl₃ as precursor) followed by calcination at 673K for 4 hours.
a) Au/P25 (0.6wt% Au)  
Particle size ~2-7 nm.

b) Au/Hombicat (0.6wt% Au)  
Particle size ~9-24 nm.

c) Au/Hombicat (2.0 wt% Au)  
Particle size ~13-35 nm.

Figure 18: TEM images of calcined Au/TiO$_2$ catalysts

The dark spots in the images represent the gold particles on the TiO$_2$ surface. The Au/P25 catalyst is used as reference, because Nijhuis and Zwijnenberg studied the same catalyst. The TEM image of the 0.6wt% Au/P25 catalyst (Figure 18a) shows particles well dispersed with sizes in the range of 2-7 nm. This is in line with the results of Nijhuis and Zwijnenburg [12,13] who reported dispersion of 3-10 nm. TEM images shows that Hombicat has another morphology than Degussa P25. Furthermore, the Au particles on the Hombicat surface are much larger (9-24 nm in Figure 18b) compared to the same gold loading on Degussa P25. When the gold loading is increased to 2 wt% Au, the particles also increases in size (13-35 nm in Figure 18c).

4.1.2.2. Catalysts obtained by chemical reduction.

In Figure 19 the TEM images are given of catalysts prepared by chemical reduction. These catalysts are prepared by deposition-precipitation of Au(OH)$_3$ (with AuCl$_3$ as precursor) followed by chemical reduction with NaBH$_4$. The first images show the surfaces of each catalyst after gold deposition, but before the reduction step. The second images are taken after reduction.
Again Au/P25 is used as reference, because Dimitratos also studied the same catalysts. Figure 19a shows particles sizes of around 1 nm before reduction and 3-6 nm after reduction, which is similar to the results of Dimitratos. The other three catalysts show comparable results as for P25; sintering of Au nano-particles occurs during chemical reduction. The 1 nm particles visible before reduction are most likely Au salt nano-particles. Unfortunately, it was not possible to prove this with Energy Dispersive X-ray analysis (EDX) due to the small size. EDX taken after reduction does confirm the presence of gold. The large coagulates in the gold/Aldrich catalyst (Figure 19d bottom) are the results of a too high gold loading (2 wt%).

### 4.1.3. RAMAN.

The photocatalytic activity is influenced by the support properties. As mentioned in the chapter “Theoretical Considerations”, anatase and rutile has different band gap energies, which results in different activity of the catalyst. Therefore the original structure is determined by using Raman spectroscopy. Raman spectra were measured employing Ramanscope provided by RENISHAW®.

The Raman spectra identify the anatase and rutile phases of the samples. Table 7 represents the bands belonging to respectively the anatase and rutile structure [29].
Table 7: Raman bands for anatase and rutile phase [29]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>144 197 399 515 519 639</td>
</tr>
<tr>
<td>Rutile</td>
<td>143 235 447 612</td>
</tr>
</tbody>
</table>

![Raman spectra of pure TiO$_2$ catalysts](image)

**Figure 20:** Raman spectra of pure TiO$_2$ catalysts

![Raman spectra of Au/TiO$_2$ catalysts](image)

**Figure 21:** Raman spectra of Au/TiO$_2$ catalysts (only chemical reduced samples).

Both Figures (Figure 20, 21) show peaks at anatase spectra bands, but the Degussa P25 samples are also showing a small peak at 447 cm$^{-1}$, indicating that also a rutile phase is present. This was already
known from the data delivered by the TiO$_2$ manufactures. The peak at 170 cm$^{-1}$ in the Hombicat spectra is not fully understood, there might be some interferences with other peaks. XRD might deliver more information about the influences of gold deposition on the composition of TiO$_2$ (anatase/rutile). This will be discussed in the next paragraph.

4.1.4. XRD.

X-ray diffraction (XRD) is used to determine the structure of solids and is a widely used technique. The XRD patterns were measured at a Philips PW 1840 diffractometer equipped with a graphite monochromator using Cu-K$_\alpha$ radiation ($\lambda = 0.1541$ nm).

The results of the XRD analysis are presented below in groups based on their TiO$_2$ support. The influences of the activation step between the two methods will be discussed.

The XRD patterns of anatase and rutile can be separated by their different characteristic peaks. Table 8 indicates which diffraction angle corresponds with 2*theta for anatase and rutile structures.

Table 8a: Diffraction angles and corresponding XRD angles of Anatase.

<table>
<thead>
<tr>
<th>Diffraction angles</th>
<th>(004)</th>
<th>(004)</th>
<th>(200)</th>
<th>(105)</th>
<th>(211)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2*theta</td>
<td>25.5°</td>
<td>37.9°</td>
<td>48.2°</td>
<td>53.8°</td>
<td>55.0°</td>
</tr>
</tbody>
</table>

Table 9b: Diffraction angles and corresponding XRD angles of Rutile.

<table>
<thead>
<tr>
<th>Diffraction angles</th>
<th>(101)</th>
<th>(110)</th>
<th>(111)</th>
<th>(211)</th>
<th>(002)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2*theta</td>
<td>27.6°</td>
<td>36.1°</td>
<td>41.2°</td>
<td>54.3°</td>
<td>62.7°</td>
</tr>
</tbody>
</table>

The rutile peak at 2\(\theta\) = 54.3° is very hard to be detected, because it might be overlapped by the anatase peaks in that region of the XRD pattern (2\(\theta\) = 53.8° and 55.0°).

To estimate the fraction of anatase and rutile in the obtained samples, the weight percentage of the anatase phase, $W_A$, was determined using the following equation [30]:

$$W_A = \frac{1}{1 + 1.265 \frac{I_R}{I_A}}$$

$I_A$ denotes the intensity of the strongest anatase reflection and $I_R$ is the intensity of the strongest rutile reflection. The ratio $I_A/I_R$ is independent of fluctuations in the diffractometer characteristics. A prerequisite to use this equation is that the peak of the anatase or rutile phase has to be clearly visible in the XRD pattern.
4.1.4.1. Degussa P25 catalysts.

Information from the manufacturer reveals that Degussa P25 TiO$_2$ consists of approximately 70% anatase and 30% rutile. Therefore, both these structures of TiO$_2$ should be observed in the XRD pattern of Degussa P25.

![Figure 22: XRD patterns of P25 and Au/P25 catalysts.](image)

The three samples show similar XRD patterns. Figure 22 shows peaks at $2\theta = 25.3^\circ$ and $48.1^\circ$, and are typically indicating the presence of the anatase structure. The peaks at $2\theta = 27.4^\circ$ and $41.3^\circ$ indicates the presence of rutile. For all three samples, the intensity of anatase peak at $2\theta = 25.3^\circ$ was considered as $I_A$ and the intensity of rutile peak at $2\theta = 27.4^\circ$ was considered as $I_R$. The calculated results of $W_A$ for all samples are shown in Table 10 (also in Appendix 13). It indicates that the chemical reduced gold/titania catalyst has the same fraction (72.5 wt%) of anatase phase as the Degussa P25 support (without gold) and that the gold deposition has no influences on the structure of Degussa P25 TiO$_2$. However, although the three XRD patterns appear to be the same, the rutile peak at $2\theta = 27.4^\circ$ of the calcined Au/TiO$_2$ catalyst has a lower intensity, resulting in a higher weight percentage of the anatase phase (74.6 wt%). This is an unexpected result, because the anatase structure is known as the unstable phase.

<table>
<thead>
<tr>
<th>Table 10: Crystal structure of P25 and Au/P25 catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>P25</td>
</tr>
<tr>
<td>Au/P25 (chem. red.)</td>
</tr>
<tr>
<td>Au/P25 (calc.)</td>
</tr>
</tbody>
</table>

4.1.4.2 Hombicat.

Hombicat UV 100 (Sachtleben) consists of 100% anatase phase [6] (Suppliers data). Compared to the XRD patterns of Degussa P25, the peaks of Hombicat (Figure 23) are wider due to the smaller particle sizes of TiO$_2$. The line broadening indicates a decrease of the average particle dimensions. The smaller the particle, the broader and lower the peak will be.
In Figure 23, the bottom two XRD patterns are from the not-calcined catalysts; they show similar patterns. The peaks at $2\theta = 25.4^\circ$, $38.0^\circ$ and $48.1^\circ$ show the presence of the anatase structure. The peak around $2\theta = 54.7^\circ$ is very wide, due to two anatase peaks ($53.8^\circ$ and $55.0^\circ$) overlapping each other. Therefore, it could not determined if there is a rutile peak ($54.3^\circ$) present. But from the absence of the specific rutile peaks at other diffraction angles, it is believed that, as expected, no rutile structures are present.

The XRD patterns of the three calcined catalysts are the top three patterns of Figure 19. The left three anatase peaks in the patterns are the same as described before, only the peaks become a bit narrower due to large crystalline particles. This also causes peak splitting in the wide peak around $2\theta = 54.7^\circ$, resulting in two peaks which has still a small overlap. The peaks are situated at $2\theta = 54.1^\circ$ and $55.1^\circ$. The peak at $2\theta = 55.1^\circ$ is certainly an anatase peak, but the peak at $2\theta = 54.1^\circ$ is believed to be a rutile peak. The intensity of this rutile peak at $2\theta = 54.1^\circ$ was considered as $I_R$ and the intensity of anatase peak at $2\theta = 25.4^\circ$ was considered as $I_A$.

**Table 11: Crystal structure of Hombicat and Au/Hombicat catalysts.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombikat</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>Hombikat (calc.)</td>
<td>87.7%</td>
<td>12.3%</td>
</tr>
<tr>
<td>Au/Hombi (chem. red.)</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>Au/Hombi (0.6wt% calc.)</td>
<td>84.8%</td>
<td>15.2%</td>
</tr>
<tr>
<td>Au/Hombi (2wt% calc.)</td>
<td>81.5%</td>
<td>18.5%</td>
</tr>
</tbody>
</table>

Table 11 shows the calculated results of $W_A$ for all samples. The composition of the not-calcined catalysts are considered 100% anatase. The Table indicates that calcination changes the composition of Hombicat, which was also determined by the XRD patterns due to the line broadening. Furthermore, the 0.6% Au/TiO$_2$ has a $W_A$ value (84.8%) lower than that (87.7%) of the pure calcined
TiO$_2$, followed by 2.0%Au/TiO$_2$ with a $W_A$ value of 81.5%. It is concluded that gold deposition increases the rutile content of the catalyst, which is confirmed by literature [19]. Remarkable is the little shoulder around $2\theta = 44^\circ$ of the calcined Au/TiO$_2$ catalysts. This could be a gold peak as reported [19] and is probably noticed due to the large gold particles on the TiO$_2$ surface due to the calcination process.

4.1.4.3. Merck and Aldrich catalysts.
The XRD patterns of Merck and Aldrich will be discussed together, because the patterns show similar peaks in the Figures (Merck Figure 24, Aldrich Figure 25).

![Figure 24: XRD patterns of Merck and Au/Merck catalysts.](image)

![Figure 25: XRD patterns of Aldrich and Au/Aldrich catalysts.](image)

Both Figures are showing XRD patterns with narrow peaks. This indicates that the crystal size is large in both TiO$_2$ supports. Most peaks are indicating anatase as main component, but the $2\theta$ of 62.7$^\circ$ is indicating the presence of rutile phase. The results (Table 12) of $W_A$ for these samples were calculated by using the intensity of anatase peak at $2\theta = 25.3^\circ$ as $I_A$ and the intensity of the rutile peak at $2\theta =$
62.7° as I_R. Again the gold deposition slightly increases the content of rutile for both cases. The anatase phase for Merck lowers from 88.4% to 88.2% and for Aldrich from 88.4% to 87.0%.

| Table 12: Crystal structure of Merck, Au/Merck, Aldrich and Au/Aldrich catalysts |
|-------------------------------|-----------------|
| Anatase          | Rutile         |
| Merck            | 88.4% 11.6%    |
| Au/Merck         | 88.2% 11.8%    |
| Aldrich          | 88.4% 11.6%    |
| Au/Aldrich       | 87.0% 13.0%    |

4.1.5. TGA.
Temperature gravimetric analysis (TGA) is used to determine thermal stability and the fraction of volatile components by monitoring the weight change that occurs as a sample is heated. The measurements are carried out in a Mettler Toledo, TGA/SDTA851e instrument and are done in air. The chosen temperatures in the temperature program were 25°C (30 min.), 120°C (4 hours), 220°C (4 hours) and 600°C (30 min.), with a temperature ramp of 5°C/min between every temperature level. For catalysts prepared by the chemical reduction method, Figure 26 show both the weight decrease as a function of time (left Y-axis) and the temperature program as a function of time (right Y-axis). The weight of the gold/TiO₂ catalysts seems to decrease somewhat more than untreated TiO₂ catalyst, probably due to remaining water and/or other volatile components that stay behind after the gold deposition procedure (e.g. dissolving the support in water).

Figure 26: Thermal gravimetric analysis of four different TiO₂-based catalysts, a. Degussa P25, b. Hombicat, c. Merck, d. Aldrich.
Table 1 in Appendix 14 gives the weight loss percentage of all samples. Hombicat samples have a large decrease in weight during the TGA measurements (around 12wt% up till 600°C). To determine which components are released, a temperature programmed desorption (TPD) followed by mass-spectroscopy is performed.

The temperature program for TPD-MS started at 25°C and ran to 600°C at a heating ramp of 10°C/min. The TPD-MS measurements are given in Appendix 15. The TPD-MS Figures of both Hombicat samples show that they lose much water and OH-groups compared to other components, like CO$_2$. This is the result of the high surface area of Hombicat combined with its high amount of OH-groups, as observed by N$_2$ physisorption and NH$_3$-TPD. These properties are much lower for the other samples and consequently the weight loss during the TGA measurements remains small in contrast to the Hombicat samples. This hypothesis is also confirmed by TGA analysis of the calcined Hombicat TiO$_2$, where the surface area and amount of OH groups are much lower than the chemical reduced Hombicat. Figure 26b shows a decrease in weight of only 5% instead of 12%.

4.1.6. UV-VIS.

Ultraviolet-visible (UV-VIS) spectroscopy is the measurement of absorption intensity of UV/VIS light by a sample. All catalyst samples were measured using a UV-Visible Spectrophotometer Cary1 from VARIAN using BaSO$_4$ as reference standard. The wavelength scan range was 190-800 nm. The absorbance spectra of the chemical reduced samples are given in Appendix 16. Figure 27 displays the percentage absorbed light against wavelength of the chemical reduced samples with Degussa P25 and Hombicat.

As can be observed, gold deposition causes additional light absorbance at higher wavelengths for all TiO$_2$ supports; around 540 nm there is an obvious peak. This indicates the catalyst can also be photocatalytic active at higher wavelengths (visible light). Furthermore, the pure Degussa P25 TiO$_2$ is showing a less steep slope than the other three pure TiO$_2$. The intersection of extrapolated lines from the slope and the tail of the absorbance spectra provide an estimation concerning the bandgap energy. For Hombicat, these two lines cross each other at 390 nm, while for Degussa P25 this point is
at 405 nm. So the band gap energy of Degussa P25 TiO₂ should be lower than that of Hombicat TiO₂ due to the presence of rutile phase.

\[ E = \frac{hc}{\lambda} \]

- \( E \) = band gap energy (eV)
- \( h \) = Planck constant, \( 4.14 \times 10^{-15} \) (eV·s)
- \( c \) = light speed, \( 3.0 \times 10^{17} \) (nm/s)
- \( \lambda \) = wavelength (nm)

When the obtained wavelength values are used in this equation, the bandgap energy of Degussa P25 (3.07 eV) is lower than the band gap energy of Hombicat (3.18 eV). This is in accordance with literature. Hombicat TiO₂ consists of 100% anatase, which has a band gap of 3.2 eV. Degussa P25 TiO₂ consists of 27.5% rutile (XRD) and rutile has a band gap of 3.0 eV [31].
4.2. Photo oxidation of cyclohexane to cyclohexanone.

4.2.1. Results.

Most prepared catalysts were studied in the photo oxidation of cyclohexane to cyclohexanone using the immersion well reactor as described in the paragraph Experimental. The catalyst studied are depicted in Table 13 and includes the characteristic catalyst properties as measured and reported in the previous paragraph.

<table>
<thead>
<tr>
<th>Activation method</th>
<th>Au (%)</th>
<th>Au particle size (nm)</th>
<th>OH groups (mmol/g)</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt;, (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
<th>Anatase, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombicat</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcined, 673 K</td>
<td></td>
<td></td>
<td>0.66</td>
<td>160</td>
<td>87.7</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>9-24</td>
<td>0.62</td>
<td>156</td>
<td>84.8</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>13-35</td>
<td>0.63</td>
<td>147</td>
<td>81.5</td>
</tr>
<tr>
<td>Chem. reduced</td>
<td></td>
<td></td>
<td>0.90</td>
<td>337</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4-10</td>
<td>0.88</td>
<td>317</td>
<td>100</td>
</tr>
<tr>
<td>Degussa P25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chem. reduced</td>
<td></td>
<td></td>
<td>0.30</td>
<td>51</td>
<td>72.5</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3-6</td>
<td>0.19</td>
<td>49</td>
<td>72.4</td>
</tr>
<tr>
<td>Merck</td>
<td></td>
<td></td>
<td>n.d.</td>
<td>11</td>
<td>88.4</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5</td>
<td>0.06</td>
<td>11</td>
<td>88.2</td>
</tr>
</tbody>
</table>

The results of the photo oxidation, i.e. the production of cyclohexanone and cyclohexanol and the selectivity as function of irradiation time are given in Figure 28 – 36. Carbon dioxide development is also given for the experiments where the carbon dioxide formation was determined (chemically reduced catalysts). The photonic efficiency is also plotted against radiation time and is given in Appendix 17.

![Figure 28: (a) Product development and (b) selectivity of calcined Hombicat catalyst during photo-oxidation of cyclohexane.](image)
Figure 29: (a) Product development and (b) selectivity of calcined 0.6wt% Au/Hombicat catalyst during photo-oxidation of cyclohexane.

Figure 30: (a) Product development and (b) selectivity of calcined 2.0wt% Au/Hombicat catalyst during photo-oxidation of cyclohexane.

Figure 31: (a) Product development and (b) selectivity of Hombicat catalyst during photo-oxidation of cyclohexane.
Figure 32: (a) Product development and (b) selectivity of chemical reduced 1wt% Au/Hombicat catalyst during photo-oxidation of cyclohexane.

Figure 33: (a) Product development and (b) selectivity of P25 catalyst during photo-oxidation of cyclohexane.

Figure 34: (a) Product development and (b) selectivity of chemical reduced 1wt% Au/P25 catalyst during photo-oxidation of cyclohexane.
Figure 35: (a) Product development and (b) selectivity of Merck catalyst during photo-oxidation of cyclohexane.

Figure 36: (a) Product development and (b) selectivity of chemical reduced 1wt% Au/Merck catalyst during photo-oxidation of cyclohexane.

All experiments show the same trends in product formation. The formation of cyclohexanone has a high initial rate in the first 60-80 minutes. After this initial stage a decrease of cyclohexanone formation is visible. For the calcined catalysts this decrease in formation rate appears to be larger than for chemically reduced catalysts. Furthermore, the formation of cyclohexanone is larger than that of cyclohexanol, which results in a high selectivity to the ketone. This is not the case for Merck and Au/Merck catalysts, which show much lower activity and selectivity to cyclohexanone.

4.2.2. Discussion.

4.2.2.1. Selectivity cyclohexanone/cyclohexanol.

All photo oxidation reactions show that the formation of cyclohexanone prevails over that of cyclohexanol, except for the Merck catalyst. In Table 14, the selectivity for each catalyst is depicted.
Table 14: Selectivity cyclohexanone/cyclohexanol for various catalysts

<table>
<thead>
<tr>
<th>Activation method</th>
<th>Au (wt%)</th>
<th>Selectivity ketone/alcohol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombicat</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcined, 673 K</td>
<td>-</td>
<td>96</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>Chem. reduced</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>89</td>
</tr>
<tr>
<td>Degussa P25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chem. reduced</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>91</td>
</tr>
<tr>
<td>Merck</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chem. reduced</td>
<td>-</td>
<td>49</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>55</td>
</tr>
</tbody>
</table>

The low selectivity of the photo oxidation with Merck catalysts is probably due to the very different catalyst characteristics compared to the other catalysts. The very low amount of active OH-group and very low surface area will play an important role in the poor activity towards ketone formation. This condition might be compared with the conditions Du [6] reported for a Pyrex reactor filled without any catalyst, resulting in some formation of cyclohexanol due to photolysis by remaining deep UV light. Only 95% of deep UV light is cut off by the Pyrex glass and the remaining 5% cause photolysis and results in formation of cyclohexanone (see Figure 7).

4.2.2.2. Reaction kinetics.

The cyclohexanone and cyclohexanol formation by photo oxidation is assumed to occur in two reaction loops, one loop for cyclohexanone formation and another for catalytic photo-oxidation to cyclohexanol (Figure 37). In the second loop cyclohexanol is oxidized into carboxylates, blocking the active -OH sites and thus deactivating the catalyst. Only further oxidation to carbondioxide leads to reactivation of the photo catalyst. Besides the catalytic formation of cyclohexanol, there also might be straight photolytic oxidation of cyclohexane to cyclohexanol as reported by Du. Which reaction of cyclohexanol formation prevails is not studied in this MSc project.
In all Figures, the initial reaction rate of cyclohexanone formation is significantly higher than the reaction rate in the end. After 45-60 minutes of irradiation the reaction rate decreases tremendously by a factor 4-6 and even with a factor 13 to 20 for the experiments with the calcined Hombicat catalysts.

It appears that the photo oxidation with TiO$_2$ catalysts can be described by two reaction stages, i.e. an initial stage and a steady-state stage. After the initial stage, ending after 45-60 minutes, the reaction rate decreases which is assumed due to deactivation of the catalyst by oxidation of cyclohexanol to carboxylates, as described by the second reaction loop. These carboxylates are blocking active sites for further cyclohexanone formation. The initial stage can be described to be the stage where initially all active sites are available for cyclohexanone formation, while steadily the apparent slower second loop forms carboxylates and deactivates the catalyst more and more. Subsequently, a part of these carboxylates are oxidized to carbon dioxides resulting in reactivating the catalyst. Apparently after 45-60 minutes the process of carboxylates formation and subsequent oxidation with reactivation of the catalyst has reached a dynamic equilibrium and a steady-state situation is established. It is believed that the decarboxylation is the rate determining step in the second loop.

Figure 37: Two loop reaction mechanism for photo oxidation of cyclohexane with TiO$_2$ catalyst
Table 15: Reaction rates at the initial stage and steady state stage for various catalysts.

<table>
<thead>
<tr>
<th>OH groups (mmol/g)</th>
<th>Initial rate (mol/L/min)</th>
<th>Steady state rate (mol/L/min)</th>
<th>ratio initial/steady st.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombi calc</td>
<td>0.66</td>
<td>5.6</td>
<td>0.37</td>
</tr>
<tr>
<td>Au/Hombi (0.6 wt%) calc</td>
<td>0.62</td>
<td>5.4</td>
<td>0.32</td>
</tr>
<tr>
<td>Au/Hombi (2.0 wt%) calc</td>
<td>0.63</td>
<td>3.5</td>
<td>0.16</td>
</tr>
<tr>
<td>Hombicat</td>
<td>0.90</td>
<td>7.1</td>
<td>1.52</td>
</tr>
<tr>
<td>Au/Hombi (chem red)</td>
<td>0.88</td>
<td>5.9</td>
<td>1.31</td>
</tr>
<tr>
<td>P25</td>
<td>0.30</td>
<td>7.0</td>
<td>1.46</td>
</tr>
<tr>
<td>Au/P25 (chem red)</td>
<td>0.19</td>
<td>4.9</td>
<td>1.12</td>
</tr>
</tbody>
</table>

4.2.2.3. Effect of gold deposition.

Table 15 and Figures 38-41 show all a decrease of both the initial as steady state reaction rate when the catalysts are treated by gold deposition. The decrease is surprising because the stronger effect of charge separation by gold was expected to transfer more electrons to oxygen molecules resulting in stronger oxidation properties of the gold containing catalysts. However, the hypothesis is that the same mechanism is responsible for an increase in the kinetics for the second loop, which promotes deactivation. Apparently, the reaction for reactivation by decarboxylation remains the rate-determining step.

![Figure 38: Cyclohexanone formation over calcined Hombicat and Au/Hombicat.](image1)

![Figure 39: Cyclohexanone formation over chemical reduced Hombicat and Au/Hombicat.](image2)
As recommendation for further research decarboxylating promoting conditions has to be studied, because when the decarboxylation is not the rate limiting reaction step anymore, the higher initial reaction rate would be maintained.

That deactivation plays an important role in the explanation why gold deposition leads to a decrease, in stead of an increase, of the photocatalytic activity of the photo oxidation of cyclohexane to cyclohexanone is supported by the following findings:
   a) Carbon dioxide formation
   b) TGA results and IR spectra of catalysts before and after photo oxidation

\textit{a) Carbon dioxide reaction rate.}

For both the Hombicat as Degussa P25 catalysts the gold deposit has lower rates of carbon dioxide formation in the steady state stage. (Figures 42-44 and Table 16). This indicates a lower decarboxylation rate for catalysts with gold, and therefore a higher percentage of active sites which remain blocked compared to the catalyst without gold. Consequently, gold deposition reduces the decarboxylation reaction kinetics which supports the hypothesis that slower decarboxylation (the rate limiting step in the steady state stage) slows down cyclohexanone formation as is the case when TiO$_2$ catalysts have gold deposit.
Figure 42: CO$_2$ development over (a) Hombicat and (b) Au/Hombicat

Figure 43: CO$_2$ development over (a) P25 and (b) Au/P25

Figure 44: CO$_2$ development over (a) Merck and (b) Au/Merck
Table 16: Carbon dioxide formation rates as measure for decarboxylating of active catalyst sites

<table>
<thead>
<tr>
<th></th>
<th>Activation method</th>
<th>Au (wt%)</th>
<th>CO₂ formation rate (mmol/L/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombicat</td>
<td>Chem. reduced</td>
<td>-</td>
<td>3.71·10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>3.58·10⁻³</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>Chem. reduced</td>
<td>-</td>
<td>3.77·10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>1.92·10⁻³</td>
</tr>
</tbody>
</table>

b) TGA results and IR spectra of catalysts before and after photo oxidation.

The TGA of Hombicat catalyst with gold deposit after the photo oxidation experiments indicate a loss of components at three temperatures, i.e. at 225°C, at 350°C and at 550°C (Figure 45). These peaks are attributed to oxidation of alkoxy- and carbonate carboxylates, which were verified by IR spectra (Figure 46). The amount of carboxylates is considerably higher for the catalysts with Au deposit, confirming the higher deactivation for catalyst with gold deposit.

Similar TGA and IR spectra analysis of the same catalysts before photo oxidation with and without gold deposit does not show both the presence of these carboxylates and the loss of components at the reported temperatures.

Figure 45: TGA results of fresh and spent Hombicat and Au/Hombicat catalysts.
4.2.2.4. Effect of type of TiO\textsubscript{2} support.

As seen from Figures 32-33 both the initial and steady state reaction rates as well as the photonic efficiency (Appendix 17) of P25 and Hombicat are not very different, although the surface area and amount of OH-groups of P25 would expect much lower values. Apparently, also other catalyst properties influences the production rate of cyclohexanone in the photo-oxidation of cyclohexane. For example, at pores diameters between 1 and 40 nm, internal diffusion of the cyclohexane and product molecules might be limited (Knudsen diffusion). Schematically this is represented in Figure 47.

Figure 46: IR spectra analysis of spent Hombicat and Au/Hombicat catalysts.

Figure 47: Schematic representation of reduced diffusivity in pores of catalyst
The smaller pore diameters reduce the effective active surface and number of active sites available for surface catalyzed photo oxidation. The pore distribution of Au/P25 and Au/Hombicat is shown in Figure 48.

Figure 48: Pore distribution of all Au/Hombicat and Au/P25 catalysts.

The Au/Hombicat catalysts have micro-, meso- and macropores, but mostly consists of micropores in the range of 2-20 nm, while P25 catalysts has mainly macropores of 52 nm. The influence of activation method is most noticed for calcinations of Au/Hombicat, where the micropores has a strong presence at around 4.4 nm, due to changes in catalyst composition and texture. It is believed that chemical reduction does not change the pore characteristics a lot. Therefore, it might be concluded that Hombicat catalysts have a surface and an active site concentration, which is for a large part not available for oxidation reactions due to the diffusion-limiting micro pores of below 20 nm. From the pore distribution curve the percentage of surface cq. active sites not available for reaction can be estimated at around 40%. In Figure 49 both the effective active site concentration (open symbols) as total active site concentration is plotted (filled symbols). Still after taking into account the lower availability of active sites, the difference between P25 and Hombicat cannot be explained totally. Possibly, another property which is different between Hombicat and P25 might play a role too, i.e. the percentage of rutile. P25 has about 25% rutile, while Hombicat is almost pure anatase. The lower band gap energy of rutile (near visible light) might help the decarboxylation reaction in the second loop, which explains why despite a lower active site concentration the reaction rates for P25 might be similar to Hombicat.
4.2.2.5. Effect of Activation method.

All Hombicat-based catalysts were tested for the photo-oxidation of cyclohexane under same reaction conditions and therefore can be compared with each other.

<table>
<thead>
<tr>
<th>OH groups</th>
<th>Initial rate (mol/L/min)</th>
<th>Steady state rate (mol/L/min)</th>
<th>Ratio initial/steady st.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombi calc 673 K</td>
<td>0.66</td>
<td>5.6</td>
<td>0.37</td>
</tr>
<tr>
<td>Hombicat</td>
<td>0.90</td>
<td>7.1</td>
<td>1.52</td>
</tr>
</tbody>
</table>

The calcined catalyst has a smaller initial reaction rate due to its lower surface area and amount of OH-groups. The reduction of the initial rate is almost proportional to the decrease of active sites. Furthermore, the calcined catalyst has more and faster deactivation during reaction time as clearly shown in the larger ratio of initial rate and steady state rate. As far is known, besides the difference in active sites and surface area, the pore diameter distribution is the only other parameter which differs between the calcined catalyst and the chemically reduced catalyst. Calcination “consumes” pore diameters below 3 nm for the formation of pores with an average diameter of 4.4 nm. One hypothetical explanation of the higher catalyst deactivation for calcined catalysts might be found in a more difficult/slower decarboxylation and thus lower decarboxylation rate. Unfortunately, during the photo oxidation experiments with calcined Hombicat the samples were not analysed for carbon dioxide formation.
The effect of different calcinations temperatures is seen in Figure 50.

The steady state reaction rate of the photo oxidation of cyclohexane with Hombicat catalysts calcined at different temperatures is proportional to the number of active sites and surface area as shown in Figures 50-51. The higher the calcinations temperature, the lower the reaction rate, number of active sites and surface area. The photo catalytic activity of the Hombicat is strongly reduced at higher calcinations temperatures. Therefore, calcinations is not considered as an attractive method for catalyst activation, e.g. when gold deposits has to be reduced.
4.3. Photo oxidation of Methylene Blue.

4.3.1. Results.

The decomposition of methylene blue (MB) by using several TiO$_2$-based catalysts are presented in Figures 52-55. The duplo experiments are given in Appendix 18.

For all catalysts except for pure Hombicat, the MB decomposition starts immediately after illumination. Hombicat (Figure 52) shows an initial delay in decomposition of MB; the first 30 minutes the concentration stays constant at the initial concentration. The other catalysts (Figure 53-55) show “normal” degradation profiles without any delays. Furthermore, it is clearly seen that both Aldrich as well as Au/Aldrich has fast initial degradation, slowing down after 30-40 minutes at about 60% conversion.

For all catalysts except for pure Hombicat, the MB decomposition starts immediately after illumination.
for the Aldrich-based catalysts, and the lowest for Hombicat. However, as also can be seen from the Aldrich degradation profiles, Aldrich-based catalysts takes much more time for total degradation compared to the other catalysts.

Table 18: Catalyst activity, time needed to decompose to 50% and 10% of the initial concentration.

<table>
<thead>
<tr>
<th></th>
<th>( t_{50%} ) (min)</th>
<th>( t_{10%} ) (min)</th>
<th>( \Delta t_{50%\rightarrow10%} ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombicat</td>
<td>119</td>
<td>204</td>
<td>86</td>
</tr>
<tr>
<td>Au/Homb</td>
<td>33</td>
<td>81</td>
<td>48</td>
</tr>
<tr>
<td>P25</td>
<td>26</td>
<td>83</td>
<td>57</td>
</tr>
<tr>
<td>Au/P25</td>
<td>26</td>
<td>91</td>
<td>64</td>
</tr>
<tr>
<td>Au/Merck</td>
<td>16</td>
<td>63</td>
<td>47</td>
</tr>
<tr>
<td>Aldrich</td>
<td>14</td>
<td>252</td>
<td>238</td>
</tr>
<tr>
<td>Au/Aldr</td>
<td>14</td>
<td>165</td>
<td>151</td>
</tr>
</tbody>
</table>

Gold deposition at the various catalysts appears to decrease the MB decomposition rate for Hombicat and to remain the same for P25. The Aldrich supports with gold deposits act as expected and have an increased decomposition rate in the steady state stage as compared to the pure Aldrich support.

Some introductory remarks on possible influence of the results by the experimental set-up:

- **Temperature control** has been limited to control of the box environment by an electric fan and cooling/heating tubes.
  During the irradiation and photo-oxidation heat is produced. It appeared that cooling by the box environment was not sufficient as was noticed during the experiment. Temperatures fluctuations between 30 to 35°C were detected. With these temperature fluctuations the rate constants will fluctuate about 20-30% when calculated by an Arrhenius relation with activation energy \( E_a \) of 36 kJ/mol [32] (Appendix 19).

- **No pH control.**
  In aqueous environment the adsorption behaviour of MB on the TiO\(_2\) phoyocatalysts is for a large part determined by the zeta,\( \zeta \)-potential of TiO\(_2\). In literature isoelectric points for various TiO\(_2\)-catalysts are reported at pH values ranging from 5.2 to 6.4. Mrowetz et al [33] reported an optimal photocatalytic activity at pH values close to the isoelectric point. Higher and lower pH values decrease the activity. The formation of degradation products as e.g. SO\(_3^-\) and NH\(_4^+\) might influence the pH at the TiO\(_2\) surface and consequently influencing the photo catalytic activity.
4.3.2. Discussion.

4.3.2.1. Reaction model and mechanism
Various kinetic models were proposed in literature [28,32,34]. Most studies use the Langmuir-Hinshelwood rate equation to explain the experimental results. However, when the initial concentration of the reactant is low \( C_0 = 50 \text{ ppm} \), the Langmuir-Hinshelwood equation can be simplified and the rate becomes pseudo first order [35].

\[
C(t) = C_0 \cdot \exp(-k_{app}t)
\]

\( C_0 \) and \( C(t) \) are the concentrations of the dye (MB) at respectively time 0 and t, and \( k_{app} \) is the apparent rate constant, which includes various parameters such as the mass of catalyst, the flux of efficient photons, the coverage in oxygen and adsorption constant.

Wu et al. [32] proposed a mechanism, where dye adsorption at the TiO\(_2\) surface (eq. 1) is followed by the formation of hydroxyl radicals and super oxide radicals (eq 2-5). The OH radical and the O\(_2\) radical will attack the adsorbed MB (eq. 6-7) and will decompose it into intermediate products and degradation products.

1. \( TiO_2 + MB \leftrightarrow TiO_2 - MB \)
2. \( TiO_2 - MB + h\nu \leftrightarrow TiO_2(e^-, h^+) - MB \)
3. \( h^+ + (HO)_ads \rightarrow (OH)_{ads}^\cdot + H^+ \)
4. \( h^+ + (OH^-)_{ads} \rightarrow (OH)_{ads}^\cdot \)
5. \( e^- + (O_2)_{ads} \rightarrow (O_2^)_{ads}^\cdot \)
6. \( (OH)_{ads}^\cdot + MB \rightarrow \text{intermediates} \)
7. \( (O_2^)_{ads}^\cdot + MB \rightarrow \text{intermediates} \)

As already discussed, MB is decomposed into intermediate products which are colourless. However, these colourless intermediates will degrade further, which also require hydroxyl radicals and super oxide radicals (eq.8-9).

8. \( (OH)_{ads}^\cdot + \text{intermediates} \rightarrow \text{degradation products} \)
9. \( (O_2^)_{ads}^\cdot + \text{intermediates} \rightarrow \text{degradation products} \)

Schematically, a two-cycle model is proposed, involving a MB decomposition cycle and a cycle with decomposition of degradation products. Within both cycles two decomposition pathways are
described; one for the reaction with superoxide radicals and the other with hydroxyl radicals. The proposed two-cycle model is presented in Figure 56.

![Two-cycle model](image)

**Figure 56:** Two-cycle model; bottom cycle: MB decomposition, Top cycle: degradation products cycle ($P_x = P_1, P_2, P_3$, etc.).

The reaction rates of the various steps in the two-cycles will determine the curvature of the decomposition rate of MB as function of illumination time. Various steps in the cycles are competing for oxygen and active sites, while the many degradation products might influence steps in the MB decomposition cycle.

The linear transforms $\ln(C_0/C_t) = k_{app}t$ of the curves in Figures 52-55 are given in Figure 57-60. For some catalysts two stages of decomposition of MB can be seen, an initial stage and steady state stage. The linear slope of each stage correspond with the apparent rate constants ($k_{app}$) and are given in Table 19.
Table 19: The initial and steady state apparent rate constant and the amount of surface hydroxyl groups.

<table>
<thead>
<tr>
<th></th>
<th>Initial $k_{app}$ (min$^{-1}$)</th>
<th>Steady state $k_{app}$ (min$^{-1}$)</th>
<th>OH groups (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombicat</td>
<td>0</td>
<td>2.75·10$^{-2}$</td>
<td>0.92</td>
</tr>
<tr>
<td>Au/Hombicat</td>
<td>1.74·10$^{-2}$</td>
<td>1.74·10$^{-2}$</td>
<td>0.88</td>
</tr>
<tr>
<td>P25</td>
<td>3.19·10$^{-2}$</td>
<td>3.19·10$^{-2}$</td>
<td>0.30</td>
</tr>
<tr>
<td>Au/P25</td>
<td>1.87·10$^{-2}$</td>
<td>1.87·10$^{-2}$</td>
<td>0.19</td>
</tr>
<tr>
<td>Au/Merck</td>
<td>3.49·10$^{-2}$</td>
<td>1.54·10$^{-2}$</td>
<td>0.06</td>
</tr>
<tr>
<td>Aldrich</td>
<td>3.32·10$^{-2}$</td>
<td>0.49·10$^{-2}$</td>
<td>0.06</td>
</tr>
<tr>
<td>Au/Aldrich</td>
<td>2.84·10$^{-2}$</td>
<td>1.07·10$^{-2}$</td>
<td>0.06</td>
</tr>
</tbody>
</table>
The reaction rate constants in the initial and the steady state stage are similar for P25, Au/P25 and Au/Hombicat. In the Figures, where $k \cdot t$ is plotted against time ($t$) this results in a linear relation (straight line).

4.3.2.1. Effect of support.

All catalysts show fast decomposition in the initial stage (around $3 \times 10^2$ /min). Surprisingly, the decomposition rate in the initial stage is almost the same for all catalysts, although the active site concentration is quite different (factor 15 maximum). Apparently, the rate of decomposition is independent on the active sites concentration. Therefore, it is assumed the MB adsorption step on the TiO$_2$ surface of the catalyst (Equation 1) is the rate determining process of MB decomposition by photo oxidation in the initial state.

Two remarkable effects of the catalyst supports were seen, i.e. 1. a two stage oxidation process for Merck and Aldrich catalysts and 2. an initial delay of decomposition for pure Hombicat.

Ad.1. The two stage process effects into a clear reduction of decomposition rate by a factor 3-8 after 30-40 minutes. Apparently, during photo oxidation the degradation products from the second cycle, which are more polar and have higher diffusivity compete more and more for the adsorption sites. At a certain time (30-40 minutes) the degradation products have been produced in abundance and the desorption of these degradation products has become rate limiting. Consequently, a fast initial stage of decomposition is followed by a slower steady state stage. This effect is found for Aldrich and Merck catalysts only, because the number of active sites available for adsorption is reported to be 5-15 times lower than for P25 and Hombicat catalysts. Therefore, the desorption of degradation products is becoming much earlier rate limiting. Consequently, for P25 and Hombicat the decomposition rate remains constant until high conversion, while Aldrich and Merck catalysts have a decrease of decomposition rate after a certain time.

Ad.2. The initial delay for pure Hombicat suggests that for a period of time there is lack of reactant. This might be explained by the presence of sulphites in the commercially available Hombicat catalyst. Sulphites are known for its anti-oxidant characteristics and industrially known as oxygen scavengers (e.g. water treatment in boilers and wine) XRF data confirm that Hombicat contains impurities as sulphites to about 0.3 wt % (Table 20), while no sulphites were detected in the other supports. Sulphites are soluble in water and might migrate to the TiO$_2$-catalyst surface. It could desaturate O$_2$ from the surface and moreover it might “eat” the radicals formed by photo-oxidation. This corresponds with elimination of the superoxide pathway (O$_2$) and the hydroxyl pathway in the two-cycle mechanism, which results in no reaction at all. After about 60 minutes most surface sulphites are consumed and after a period of time when the decomposition of methylene blue started, the apparent rate constant will reach the steady state stage, as seen in Figure 57.
Table 20: Trace compounds at Hombicat, P25 and Merck. Determined by XRF.

<table>
<thead>
<tr>
<th>Trace compounds [wt%]</th>
<th>Na₂O</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>ZrO₂</th>
<th>V₂O₅</th>
<th>MoO₃</th>
<th>Nb₂O₅</th>
<th>I</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombicat</td>
<td>0.056</td>
<td>-</td>
<td>0.313</td>
<td>0.029</td>
<td>0.366</td>
<td>-</td>
<td>0.051</td>
<td>0.284</td>
<td>0.295</td>
<td></td>
</tr>
<tr>
<td>P25</td>
<td>-</td>
<td>-</td>
<td>0.035</td>
<td>0.011</td>
<td>-</td>
<td>0.387</td>
<td>-</td>
<td>0.379</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Merck</td>
<td>0.046</td>
<td>0.204</td>
<td>0.269</td>
<td>0.364</td>
<td>0.035</td>
<td>0.41</td>
<td>-</td>
<td>0.052</td>
<td>0.105</td>
<td>-</td>
</tr>
</tbody>
</table>

This sulphite hypothesis is supported by the absence of any delay for photo oxidation with Au/Hombicat catalysts which exhibits 4 times lower sulphite concentrations. Most probably this is due to the gold deposition procedure, where the sulphites are dissolved in water and washed off from the TiO₂ surface.

Moreover, besides the two effects of catalyst support another surprising finding relates to the lower steady state rate constant of Hombicat compared with P25, although the concentration of active sites and the specific surface area are significantly larger for Hombicat. It is believed that Hombicat have lower rate constant due to diffusion limitation, where the MB molecule (1.5nm) diffuses much slower through the micropores of Hombicat (4nm) than through the pores of P25 (52nm). The presence of diffusion limitation is confirmed by calculations of Φ, the Weisz-Prater criterion determining diffusion limitation. At values of Φ below 0.15, no diffusion limitation is expected [41]. Even at the most favorable conditions the calculated Φ values are minimal 0.3; details of the calculation are given in Appendix 20. The result of diffusion limitation is slow adsorption of MB onto the TiO₂ surface, step 1 in the reaction model. Moreover the constant migration of low amounts of sulphite might reduce the decomposition rate too.

4.3.2.3. Effect of gold deposition.

Gold deposition on the various catalysts had different effects on the MB decomposition rate. For the Hombicat and Degussa P25 TiO₂ catalysts, gold deposition leads to lower decomposition rates, while for Aldrich TiO₂ catalysts it leads to the expected increase of decomposition rate. For Hombicat and P25 this lower rate is believed to be the direct or/and indirect effect of a lower active site concentration, in combination with limited diffusivity of MB due to pore diameter restrictions. Last argument is especially applicable for Hombicat.

In more detail: The Au/P25 catalyst has significantly lower active sites concentration (33%) than pure P25. This finding is significantly different for the other catalysts, where chemical reduction by NaBH₄ had minor effect on active site concentration, pore structure and pore dimensions. Apparently, the chemical reduction of Au³⁺ for Au/P25 has a large influence on the reactive sites. More than 30% of the sites are inactivated as measured by NH₃-TPD. Most probably also the other active sites are more or less effected by chemical reduction in such a way that the MB adsorption on the active sites is negatively influenced. E.g Sodium poisoning could be one of the possibilities. Consequently, Au
deposition has two effects which are counteracting on the decomposition rate, i.e. firstly the effect of the gold nanoparticle giving a better charge separation between hole and electron, which accelerates the superoxide and hydroxyl radical pathways and secondly more difficult adsorption of MB, which slows down the rate determining MB adsorption. Consequently, the decomposition rate of MB for Au/P25 catalysts is lower than for pure P25. A similar reasoning might hold for the lower decomposition rate for Au/Hombicat catalysts.

Furthermore, the results for Au/Aldrich catalyst supports this argumentation. For Au/Aldrich the amount of active sites is the same as for pure Aldrich catalyst. However, in steady state, the gold deposition has an enormous influence on the decomposition rate (two times higher). The charge separation results in higher OH and O$_2$ radical formation, which lead to faster decomposition of MB (and also degradation products).

In conclusion: gold deposition will influence the rate of decomposition of methylene blue positively, due to the better charge separation of electrons and holes. However, several other properties of the catalyst are (more) important to consider, because they might lower the decomposition rate to a larger extent than the gain through better charge separation. Mentioned deteriorating properties are:

- Contamination of impurities, like sulphites.
- Pore distribution of the catalyst particles, where micropores leads to diffusion limitation.
- Amount of active OH sites.
- Modification or blocking of active sites, resulting in lower adsorption rate
4.4. Propane /Propylene photo-oxidation.

4.4.1. Introduction.
Some preliminary experiments for the photo oxidation of propane and propylene, using Au/P25 calcined catalysts, were performed.

Gold is known as a surface plasmon, which influences the visible light sensitivity positively [36]. To identify catalytic activity of Au/TiO$_2$ catalysts with light in the visible range, the oxidation of propane with O$_2$ to acetone is performed at several wavelengths.

Zwijnenburg [13] and Nijhuis [12] reported a high selectivity to propylene oxide for the oxidation of propylene over Au/TiO$_2$ catalysts at temperatures in the range of 348 K to 423 K using a combination of H$_2$ and O$_2$ as oxidation mixture. Oxygen and hydrogen are activated by the Au/TiO$_2$ catalyst surface and undergoes Ti-OOH formation on the surface of TiO$_2$ [13]. Propylene interacts with the perhydroxyl group on the TiO$_2$ surface resulting in propylene oxide formation.

\[
\begin{align*}
O_2 + H_2 & \xrightarrow{\text{Temp.}} OOH \\
& \xrightarrow{\text{Au}} Ti + \text{propylene} \\
\text{Propylene oxide}
\end{align*}
\]

In this study it has been suggested that perhydroxyl groups might be formed too during photo-oxidation of propylene with water, due to the presence of Au/TiO$_2$ and UV light. If that is true, direct photo-oxidation of propylene with water to propylene oxide should mean a scientific breakthrough.

\[
\begin{align*}
H_2O & \xrightarrow{hv} OOH \\
& \xrightarrow{\text{Au}} Ti + \text{propylene} \\
\text{Propylene oxide ??}
\end{align*}
\]

Other species, which can be formed can be acetone, n-propanol, i-propanol, 1,2-propandiol, aldehyde.

Besides the effect of gold on the perhydroxyl formation, recently Gibson reported that gold may activate the propylene molecule directly [37], without any interference of a TiO$_2$ support.

Both experiments has to be considered as some first “shots” to get an idea if catalysts with gold deposit would give reason to study photo catalysis in more detail for the use of visible light and for direct photo oxidation of propylene in presence of water to epoxies. Last reaction is quite challenging, because in nowadays industrial production of epoxies is inefficient and suffer from the production of many by-products [13].
4.4.2. Identification of species.
To identify the various products formed by oxidation of propane, IR spectra from literature are compared. Hamdy [38,39] studied selective photo-oxidation of propane over a new developed catalysts (TUD-1). High selectivity towards acetone was accomplished by irradiation at 365 nm. A typical IR spectrum after radiation is reported and shown in Figure 61.

Figure 61: FTIR spectra of adsorbed species arising from propane oxidation over TUD-1 at a) zero time (dark) and b) 100-minutes reaction. Inset: the acetone spectrum adsorbed on TUD-1.

The peak at 1685 cm\(^{-1}\) is characteristic for acetone, and corresponds with the acetone spectra shown in the inset of Figure 61. Also the CCC-signal at 1388 cm\(^{-1}\) is due to presence of acetone. The signals at 1572 cm\(^{-1}\) and 1435 cm\(^{-1}\) are carboxylates and at 1630 cm\(^{-1}\) is due to the presence of water. The peaks of these three components are overlapping each other. Therefore, these species are also shown after deconvolution in Figure 62.
Figure 62: IR spectrum after 100-minutes reaction over TUD-1 and its typical deconvolution into three main contributions: acetone, water and carboxylate species.

Several IR spectra from other studies are used to identify formed species during photo oxidation of propylene with water [12,13,40]. A propylene oxide IR spectrum is given below in Figure 63. The band at 1270 cm\(^{-1}\) is indicative for the symmetrical ring of propylene oxide, but is quite small. Moreover, Mul [40] reported that propylene oxide adsorption at Au/TiO\(_2\) surfaces gives a broad positive band at 3320 cm\(^{-1}\), which is lower than the band due to adsorption of propylene (3550 cm\(^{-1}\)). This shift is attributed to OH-group frequencies indicating stronger interaction with propylene oxide than propylene.

Figure 63: IR spectrum of propylene oxide
4.4.3. Results and discussion.

4.4.3.1. Propane photocatalytic oxidation with oxygen.
As depicted in Figure 64, the Au/P25 catalyst absorbs radiation above 400 nm, where pure P25 does not absorb any light. Giving the absorption in the range of visible light, photo oxidation of propane with the Au deposition at the TiO$_2$ catalyst could be expected.

![Figure 64: UV/visible spectra of Degussa P25 with and without gold deposition](image)

Figures 65-67 show the IR absorbance spectra after various time intervals during the photo-oxidation of propane/oxygen gas mixtures in the presence of Au/P25 catalyst. At the y-axis the formation of species is given in arbitrary units (a.u.).

![Figure 65: Photo catalytic oxidation of propane/oxygen gasmixture at illumination wavelength of 365 nm (catalyst Au/TiO$_2$ (Degussa P25) calcined at 400 °C for 4 hours).](image)
The Figures show a strong formation of acetone (1699 cm\(^{-1}\)), carboxylates (1574 cm\(^{-1}\)) and carbonates (1364 and 1447 cm\(^{-1}\)). The peaks at 3679, 3635, and 2363 cm\(^{-1}\) (not shown) are indicative for carbon dioxide species. A lot of water and CO\(_2\) is formed by the oxidation of propane with radiation at 365 nm. This might indicate total oxidation of propane.

The oxidation at 435 and 545 nm shows comparable results, only at much lower formation rates. When a comparison is made between 435 and 545 nm, it appears that after 25 minutes the formation rate of all species is 4-5 times lower for 545 nm; this is exemplified in the IR spectra of Figure 68 also.
The results of the formation of species are normalized to the light intensity, to compare the three wavelengths independent of the intensity of the source and are given in the column diagram in Figure 69A. Furthermore, the formation of acetone as function of wavelength is given in Figure 69B.

In conclusion:

The photo catalytic activity of the Au/P25 catalyst decreases, when radiation shifts to visible light. Although, the conversion for photo oxidation of propane in the visible light range is low, selectivity towards acetone appears to remain constant. Further research of Au/P25 assisted photo oxidation of propane to acetone in the visible light range has to be focussed on improved catalyst activity in the visible light range. Also, other photo catalytic reactions might suffer less from the drop in conversion rate at irradiation in the visible range. Moreover, depending on the reaction mechanism it could be even possible to obtain higher selectivity at higher wavelength irradiation.
4.4.3.2. Propylene photocatalytic oxidation with water.
The Au/P25 catalyst was tested if photo oxidation of propylene/water mixtures to propylene oxide at 365 nm would occur. Two mixtures were tested; Propylene (2.81 mbar) with low water pressures (0.21 mbar) and with higher water pressures (4.4 mbar). Figure 70 and 71 show the IR absorbance spectra and species formed during radiation.

![Figure 70: Photo catalytic oxidation of propylene/water mixture at illumination wavelength of 365 nm (catalyst Au/TiO\(_2\) (Degussa P25) calcined at 400°C for 4 hours); water pressure 0.21 mbar.](image)

- a. IR absorbance spectra at 10, 30 and 55 minutes.
- b. Formation of acetone, carboxylates and carbonates in first 50 min

![Figure 71: Photo catalytic oxidation of propylene/water mixture at illumination wavelength of 365 nm (catalyst Au/TiO\(_2\) (Degussa P25) calcined at 400°C for 4 hours); water pressure 4.4 mbar](image)

- a. IR absorbance spectra at 5, 20, 90, 150 and 210 minutes.
- b. Formation of acetone, carboxylates and carbonates in first 50 min

In order to check if during illumination propylene was reacting with itself, e.g. would polymerize, a blank test was done without any water (experiment not shown). No reaction products were obtained after 30 minutes illumination, as confirmed by the absence of any additional IR-absorption.
Both IR spectra show the development of acetone (1690 cm\(^{-1}\)), carboxylates (1570 and 1541 cm\(^{-1}\)) and carbonates (1452 and 1375 cm\(^{-1}\)). At wavenumbers of around 1270 cm\(^{-1}\) and around 3320 cm\(^{-1}\) (not shown) no peak development typical for propylene oxide formation could be detected. At 1270 cm\(^{-1}\) the COC stretch of the propylene oxide would be expected, while any IR absorption at 3320 cm\(^{-1}\) is attributed to propylene oxide adsorption at Au/TiO\(_2\) surface [40].

It is reported by Mul et al [40] that the band at 1451 cm\(^{-1}\) can be assigned to asymmetric CH\(_3\) stretch, but as for the IR spectra for propane oxidation it is believed that the peak at 1452 cm\(^{-1}\) is part of the peak pair assigned to carbonates. The formation of reaction products in both experiments (0.21 and 4.4 mbar water pressure) is summarized in Figure 72. At lower water pressures formation of reaction products is slower.

In conclusion:

No propylene oxide was detected during photo oxidation of propylene and water over Au/P25 catalysts. Various other reaction products are formed as acetone, carboxylates and carbonates. Lower water pressure leads to lower conversions of these reaction products.

Up till now the direct photo oxidation of propylene with water to propylene oxide appears to remain a dream, but still an interesting challenge. Further research is recommended to start closer to the condition of the experiments of Zwijnenburg; photo oxidation of propylene with O\(_2\)/H\(_2\) as oxidation mixtures.
5. CONCLUSIONS

The main goal of this project was to increase the reaction rate of the photocatalytic oxidation of cyclohexane by improving the catalyst performance, using Au/TiO$_2$ catalysts. Special focus in this project was the influence of Au/TiO$_2$ on:

- the photocatalytic activity of various oxidation reactions
- the deactivation behaviour of the catalyst and
- the oxidation reaction of organic gases in the visible light range

After this project the following can be concluded:

1. The photocatalytic activity of TiO$_2$ catalysts can be enhanced by gold deposition, but the increase of competing reactions and deactivation might have larger effects on the net photo oxidation rate. Sometimes this results in inferior kinetics when gold deposition is applied. As shown in this study, each combination of catalyst, photo oxidation reaction and environment has its own specific limitations. E.g. reaction mechanisms in liquid/gas phase or aqueous/non-aqueous could be different for the same catalyst.

2. Gold deposition by chemical reduction (NaBH$_4$) cause minor decrease of specific surface area, pore distribution and active sites of the catalyst, except for P25 where the active sites concentration decrease more than 30%. Calcination as reduction method has much larger effects on these catalyst properties. A decrease of active sites and surface area with factors 3-15 might be expected. Moreover, calcinations change the pore distribution to lower pore diameters and the crystal morphology of TiO$_2$ in favour of rutile. Both changes have a negative effect on the photo oxidation rate.

3. Compared to chemical reduction, calcination leads to larger dimensions of the gold nanoparticles, known to result in lower catalytic activity.

4. Gold deposition on the TiO$_2$ catalyst surface does not influence the high selectivity at >90% for cyclohexanone over cyclohexanol in the photo oxidation of cyclohexane

5. Most phenomena seen can be explained by a two-loop model, describing the reaction mechanism of the photo oxidation of cyclohexane to cyclohexanone and methylene blue.

6. The kinetics of the photo oxidation of both cyclohexane and methylene blue follows two stages, an initial stage at a significantly higher reaction rate than a steady state stage. In both photo oxidative reactions studied, the steady state stage is determined by rate limiting steps of decarboxylation and desorption respectively.
7. For methylene blue decomposition by photo oxidation, the active site concentration is not rate limiting in the initial stage. The adsorption of methylene blue is the rate determining step in this initial stage, while in the steady state stage the desorption of degradation products determines the overall rate.

8. Sulphites present in the TiO₂-catalysts cause a delay of photo oxidative decomposition, due to its anti-oxidant characteristics.

9. Gold deposition leads for Aldrich catalysts to a higher photo oxidation rate in the decomposition of methylene blue. The lower rates of Au/Hombicat and Au/P25 are believed to be due to a combination of lower active sites and reduced diffusivity. There are strong indications that some catalysts are exposed to Na⁺ poisoning after the NaBH₄ treatment.

10. Photo oxidation of propane to acetone appears to occur in the visible light range, although at low conversion rates.

11. The challenging idea of the possibility of direct photo oxidation of propylene to propylene oxide in the presence of water has a negative outcome. No epoxies were formed.
6. RECOMMENDATIONS

The photocatalytic activity of TiO$_2$ catalysts and its reaction mechanisms are influenced by the environment e.g. aqueous or organic and on the aggregation state (liquid or gas). Moreover, deactivation and competing reactions play a dominating role in the kinetics of photo oxidation; increasing the oxidation activity e.g. by gold deposition is not enough to enhance the kinetics.

Therefore,

1. In further studies to exploit the advantage of high selectivity of photo oxidation reactions, it is recommended to focus the research on optimisation of the specific photo oxidation process/catalyst combination. Especially, studies into ways of reducing catalyst deactivation and competing reactions would increase chance of success for higher photo oxidation rates and higher product yields. Some ideas to study are selective active sites in the catalyst surface, continuous removal of formed side products to avoid competing reactions and reaction medium that contains selective scavengers, which can prevent blockage of active sites.

2. To understand the reaction mechanism much better, research into the rate determining steps would be very helpful. E.g. analysis of adsorbed species on the catalyst surface during photo oxidation could be of interest. In-situ FTIR could be a helpful tool to follow product development in bulk and surface more accurately.

3. In further research on photo catalysis with commercial available TiO$_2$ supports, it is recommended to focus on Degussa P25 TiO$_2$ support. In comparison with Hombicat, it has much less pores with pore diameters in the range below 10nm where diffusivity limitations might occur and it has no sulphites, which might delay and influence oxidation. Compared to Aldrich and Merck the specific surface and active groups are superior.

4. Chemical reduction with NaBH$_4$ as reduction method for gold deposition is recommended, because the original catalyst properties are changed minimal. However, better understanding of Na$^+$ poisoning is necessary.

5. For tailoring specific catalyst properties, it is recommended make use of special prepared TiO$_2$ catalysts, e.g. by supercritical methods. These methods give opportunities to introduce dopants, specific groups for scavenging degradation products or reduce adsorption of degradation products, etc.

6. In aqueous environments pH control is recommended, for reasons of the large effect pH might have on adsorption characteristics of reactants and products.
7. More frequent analysis of development of oxidation products during photo oxidation, both in bulk and at the catalyst surface, would help in better understanding and confirmation of reaction mechanisms.

8. A systematic study on the effect of other noble metals or combinations on the catalyst surface would contribute to understanding how to optimise the conversion of photocatalytic oxidation of hydrocarbons.

9. The challenge to develop a direct epoxidation from propylene and water by photocatalysis has to be continued preferably by experiments “closer” to the work of Zwijnenburg and Nijhuis, i.e. photocatalysis of propylene with mixtures of H\textsubscript{2} and O\textsubscript{2}.
7. REFERENCES


8. ACKNOWLEDGMENTS

I would like to thank all the people that helped me realizing this MSc graduation project. First of all, I appreciate very much the opportunity that Prof. J. Moulijn and Dr. Guido Mul gave me to accomplish this project, although I had some limitations in presence and time available due to my rowing activities. I want to thank Prof. J. Moulijn to keep confidence in the outcome of my project and Guido for the always enthusiastic feedback and support, when I had questions or ran into problems. I am most grateful to Joana Carneiro, my daily supervisor, with whom I had so many supportive brainstorms. It was very nice working with you, I felt we formed a great team. I want to apologize for all the moments I was not there when you needed information. I am really glad that you also supported my rowing ambitions and if I reach the Olympics in Beijing you really have to come to watch!

Hiro should win a prize for the most-supportive-person of the CE group. No matter which problem or question concerning the MB set-up, immersion-wells set-up, GC analysis, etc you were always there to help. Thank you very much!

Bart and Harry, thanks for all the support concerning the chemicals, gas piping, GC apparatus and other little issues that made my work much easier.

I want to thank Patricia and Valérie for taking the TEM pictures, Sander for the N\textsubscript{2} physisorption and NH\textsubscript{3}-TPD, Ben Norder for helping me with the XRD analysis and Pascal Visser for XRF analysis.

The first “shots” experiments for propylene oxidation with water were not able to perform without all the help of Otto Berg of Leiden University. I want to show my gratitude for the 5 days-work-together and using your FTIR set-up.

A special remark is there for all people of the Catalysis Engineering group, who never made a problem, when I was on training camp or had to leave early for a rowing training. Without this support, the combination of graduation and rowing had been never possible.

My fellow students who joined me during my project in the “student room”, Johan, Dick, Harald, Martijn v.D., Michiel P., Stefan, Carlos, Roberto, Martijn S., Marco, Christian, Maarten and the two Italian chicks, it was always a nice “party” in our room. I will miss our shared complaints about reactors, GC’s, the coffee, the weather and much more.

Special thanks to my parents, who supported me during my education at the TUDelft and also traveled with me around the world during all tournaments where I competed with the Dutch national rowing team.

And last but certainly not least, dear Marianne, I think I had the most support of you, especially last year during my graduation work and tough selections for the national rowing team, you were always there and everything turned out well.
Appendices
APPENDIX 1: Number of publications versus research topics.

ScienceDirect, search for publications with keywords:

- **3891 articles**: TS = ("photocatalytic oxidation" or "photo-oxidation" or "photooxidation")
- **29 articles**: TS = ("photocatalytic oxidation" or "photo-oxidation" or "photooxidation") and "cyclohexane"
- **8 articles**: TS = ("TiO2" and ("photocatalytic oxidation" or "photo-oxidation" or "photooxidation") and "cyclohexane")
- **0 articles**: TS = ("gold/TiO2" or "Au/TiO2") and ("photocatalytic oxidation" or "photo-oxidation" or "photooxidation") and "cyclohexane")

The other photocatalytic oxidation of cyclohexane is with V$_2$O$_5$/Al$_2$O$_3$, BaY, Amorphous Silicas catalysts.
APPENDIX 2: Preparation methods for dispersed Au on TiO\textsubscript{2}.

M. Haruta / Catalysis Today 36 (1997) 153-166

Co-precipitation:
An aqueous solution of HAuCl\textsubscript{4} and a metal nitrate is poured into an aqueous solution of Na\textsubscript{2}CO\textsubscript{3} to obtain a hydroxide or carbonate co-precipitate. The precursor is washed, dried and finally calcined in air at a temperature above 250 °C.

Deposition-precipitation I (DP-I):
A metal oxide (TiO\textsubscript{2}) support is immersed in an aqueous solution of HAuCl\textsubscript{4} (pH = 6-10). Aging for 1 h results in the deposition of Au(OH)\textsubscript{3} exclusively on the surface of the metal oxide support (if concentration and temperature is properly chosen). The precursor is treated as above.

Chemical vapour deposition:
The vapour of an organic gold compound (dimethyl-gold(III)-acetyl acetonate) is introduced onto an evacuated metal oxide support. The absorbed organic gold compound is pyrolyzed in air to decompose it into small gold particles.
TEM of Au/TiO2 prepared by deposition-precipitation

N. Dimitratos et al. / Applied Catalysis A: General 311 (2006) 185-192

Immobilisation method

**System 1: PVA/NaBH₄ system**

An aqueous HAuCl₄ solution of 100µg/ml was prepared by dissolving gold (30mg) in a minimum amount of HCl/HNO₃ 3/1, v/v mixture and after removing HNO₃; it was diluted with distilled water. Maintaining the auric solution under vigorous stirring, PVA 2wt.% solution was added (PVA/Au (w/w) = 0.64); a 0.1 M freshly prepared solution of NaBH₄ (NaBH₄/Au (mol/mol) = 5) was then added to form a ruby-red metallic sol.

**System 2: THPC/NaOH system**


Sol generated as describe by Grunwaldt. A THPC solution (0.05M) is added (THPC/Au (w/w) = 0.95) to a NaOH solution (10⁻³ M) under continuous stirring. After two minutes the HAuCl₄ was added dropwise, which results in brown metallic sol.

(TRHC = tetrakis (hydroxymethyl) phosphonium chloride(P(CH₂OH)₄Cl)).

**Immobilisation on metal oxide support**

The sol was immobilised by adding TiO₂ acidified at pH 1, by sulphuric acid) under vigorous stirring and aged for 1 h. The amount of support has to be in ration to 1 wt% Au. After filtration, a colourless filtrate indicates that all the gold particles were embedded onto the TiO₂. To ensure the removal of the
material arising from the reduction treatment the sample is washed for several times. The samples are dried at 373K for 2h.

**Deposition-precipitation method II (DP-II)**
The support is dispersed in water (10ml/g) to which ammonia is added to raise the pH (9-10). NH₃ controls the pH more easily and it avoids the formation of residues of other bases. NH₃ in presents of gold salts can lead to the production of explosive fulminating gold. Over a period of two hours the required amount of gold (AuCl₃ solution) is added dropwise to the support under vigorous stirring. This mixture is stirred for another half an hour after which it is filtrated and washed with at least 10 times its own volume of distilled water. The precursor is dried in an oven overnight.

The reduction of the precursor can be carried out by two methods:

**Calcination**: The dried precursor is calcined at 723K in air for 4h.

**Chemical reduction**: The required amount of precursor is suspended in distilled water and then a solution of NaBH₄ (0.1M) is added (NaBH₄/Au (mol/mol) = 5) under vigorous stirring at room temperature. The sample is dried at 373K for 2h.

**Chemical reduction/ calcination**: Chemical reduction followed by calcination as described above.

Preparation of TiO₂ using supercritical CO₂ antisolvent precipitation (SAS) (see Appendix A)

**SAS apparatus:**

The **SAS apparatus** is well described in the article of Z.R. Tang et al.

**Catalyst preparation (exact description in article)**
The synthesis is carried out in the SAS apparatus. Supercritical CO₂ is pumped at pressures of up to 110 bar. The whole system is held at 40°C. Initially pure methanol is pumped through the fine capillary into the precipitation vessel in co-current mode with supercritical CO₂ in order to obtain steady-state conditions. After a period the liquid solvent flow is stopped and replaced by the solution of TiO(acac)₂ in methanol (13.33 mg/ml). The system pressure and temperature are kept constant during all acts. When all solution has been processed, scCO₂ is pumped for another hour to wash the vessel from
methanol condensed during the depressurization and partly solubilized the precipitated powder modified its morphology. This procedure is repeated several times till the right amount of TiO$_2$ is received. The precursor is calcined at 400°C at 2h to give scTiO$_2$.

Gold is deposit on the surface of scTiO$_2$ by deposition-precipitation. A solution of scTiO$_2$ is adjusted to pH2 by addition of dilute HCl. A HAuCl$_4$ solution is added into the slurry. The slurry is adjusted to a pH of 10 with Na$_2$CO$_3$ and stirred for 20h at room temperature. The solid is filtrated and washed until free of chlorides and then dried at 100°C overnight.

Deposition-precipitation method III (DP-III).
Several pure anatase titania powders and Degussa P25 are used as TiO$_2$ support. A HAuCl$_4$.3H$_2$O solution in water is adjusted to pH=9 by adding NaOH or KOH solution. This resulting solution is added dropwise to a stirred suspension of the support material (1g) in water (50ml). The mixture is stirred for 18h at 20°C after is adjusted to pH=9 again. The powder is filtrated and washed with 1L deionized water to ensure complete removal of chlorine ions (AgNO$_3$ test) and other weakly absorbed species. The powder is dried at 80°C in vacuum for 20h, which ensures reduction of gold. This allows the minimum Cl content in the material.
APPENDIX 3: TiO2 in photo-oxidation of cyclohexane (Du [6]).
Du found that the applied reactor material and applied amount of catalyst affects the selectivity of the oxidation of cyclohexane a lot. For photolytic oxidation (no catalyst) the selectivity to cyclohexanone is <15% and is >95% for photocatalytic oxidation.

A: No catalyst, Quartz reactor. Figure B: TiO2 catalyst, Quartz reactor. Figure C: TiO2 catalyst, Pyrex reactor. Figure D: No catalyst, Pyrex reactor.

Reactor material
Cyclohexanol seems to be the major product of uncatalyzed photooxidation of cyclohexane, in the Quartz reactor (figure A). The Quartz glass allows illumination of the reaction mixture with a wavelengths <275nm. This leads to photolysis of cyclohexane to cyclohexanol. By adding a catalyst (figure B) seems to influences the preferred reaction of cyclohexane from photolysis radical reaction to catalytic surface reaction. By changing the Quartz reactor by the Pyrex reactor (figure C) influence the concentration profile of the two products a lot. The wavelength is cut off from 275 nm, which prevent illumination of wavelengths below 275 nm. This excludes photolysis radical reactions, which results in higher cyclohexanone selectivity. The elimination of the photolysis radical reactions by using a Pyrex reactor is confirmed by figure D (no catalyst); it shows no formation of any products at all.

Slurry density
The amount of catalyst also shows to have an effect on the product distribution. The figures above indicate that in a Quartz reactor the catalytic surface reactions dominate the radical chemistry induced by photolysis by adding TiO2. Also in a Pyrex reactor it is showed that only reactions occurred when catalyst (TiO2) is added to the reaction mixture. However, there should be an optimum to the amount of added catalyst. The catalyst particles will have a great influence to induce the catalytic surface reaction, but also blocks the light that illuminates the reaction mixture and will lead to reduced reaction efficiency.
This figure shows that the TiO2 concentration in the slurry influence the production of cyclohexanone. Increase of the amount of catalyst will increase the selectivity to cyclohexanone. However, this stabilizes after a catalyst density of around 1g/L.
APPENDIX 4: Doping TiO$_2$

Doping the semiconductor with various transition metal may lead to an enhanced efficiency of the photocatalytic process. However, the photophysical mechanism of doped semiconductors is not fully understood. It is believed that the effect of doping on the photocatalytic activity is dedicated to:

- Light-absorption capability of the catalyst
- Adsorption capacity of reactant molecules at the catalyst surface
- Interfacial charge transfer rate

The light-absorption capability of the catalyst change when the colour of the catalyst goes from white to, for example, blue. Blue light is emitted from the catalyst and is not absorbed. Furthermore the adsorption capacity of reactant molecules can differ, negatively, when several transition metal are blocking the active sites of the semiconductor, positively, when it increase the adsorption strength to the catalyst. Also it increase the transfer of an electron when the electron reach the semiconductor surface and participate in oxidation and reduction reactions. The electron is donated to an electron acceptor and by increasing the velocity of this transfer the whole reaction kinetics can be improved.

Doping metals (ions) act as trapping sites for the electrons. They enhanced the recombination of photo-generated electrons and holes. Some metal ions (Fe$^{3+}$, Ru$^{3+}$, Os$^{3+}$ and Gd$^{3+}$) are known to be stable due to their half-filled electronic configuration ($d^5$ and $f^7$). This configuration is destroyed when trapping an electron and stability decreases. The electrons may easily transfer to the absorbed oxygen on the catalyst surface, which results again in the stable half-filled electron structure of the metallic ion.
APPENDIX 5: Used chemicals and compounds
Catalyst preparation

Table 1

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Supplier</th>
<th>Molar weight (g/mol)</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂ (Hombicat)</td>
<td>Sachtleben</td>
<td>79.90</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td>TiO₂ (Merck)</td>
<td>Merck</td>
<td>79.90</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td>TiO₂ (Aldrich)</td>
<td>Aldrich</td>
<td>79.90</td>
<td>n.a.</td>
</tr>
<tr>
<td>Gold chloride</td>
<td>AuCl₃</td>
<td>Aldrich</td>
<td>303.33</td>
<td>≥ 99.99 %</td>
</tr>
<tr>
<td>Ammonia hydroxide</td>
<td>NH₄OH</td>
<td>J.T.Baker</td>
<td>35.05</td>
<td>25.0%</td>
</tr>
<tr>
<td>Sodium borohydride</td>
<td>NaBH₄</td>
<td>Fluka</td>
<td>37.83</td>
<td>≥ 96%</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>-</td>
<td>18.00</td>
<td>n.a.</td>
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</table>

Immersion well reactor

Table 2

<table>
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<tr>
<th>Chemical</th>
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<th>Supplier</th>
<th>Molar weight (g/mol)</th>
<th>Purity</th>
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</thead>
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<tr>
<td>Cyclohexane</td>
<td>C₆H₁₂</td>
<td>Aldrich</td>
<td>84.16</td>
<td>99.5%</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>CH₃(CH₂)₁₄CH₃</td>
<td>Aldrich</td>
<td>226.44</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Air</td>
<td>N₂, O₂, CO₂, etc</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst</td>
<td>TiO₂ based</td>
<td>various</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Catalyst photo-activity test (methylen-blue)

Table 3

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Supplier</th>
<th>Molar weight (g/mol)</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Blue</td>
<td>C₁₆H₁₈ClN₃SₓH₂O (x = 2-3)</td>
<td>Certistain</td>
<td>319.86 (water free)</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>-</td>
<td>18.00</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst</td>
<td>TiO₂ based</td>
<td>various</td>
<td>-</td>
<td>-</td>
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</table>
Propane/propene oxidation

Table 4

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<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Supplier</th>
<th>Molar weight (g/mol)</th>
<th>Purity</th>
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<tbody>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Propene</td>
<td>C₃H₆</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>-</td>
<td>32.00</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>-</td>
<td>18.00</td>
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</tr>
<tr>
<td>Catalyst</td>
<td>TiO₂ based</td>
<td>Degussa</td>
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</tbody>
</table>
APPENDIX 6: Experimental set-up of light intensity tests.

Figure 1: Positions for photon flux measurements.

Figure 2: Photon flux measurement at, for example, position 9 for immersion-well measurements.
### APPENDIX 7: Light Intensity test results

#### Inner-well measurements

<table>
<thead>
<tr>
<th>Position</th>
<th>Photon Flux (Einstein/m²s)</th>
<th>Average Photon Flux (Einstein/m²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.98E-09</td>
<td>4.98E-05</td>
</tr>
<tr>
<td>2</td>
<td>1.03E-08</td>
<td>1.03E-04</td>
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<tr>
<td>3</td>
<td>1.21E-08</td>
<td>1.21E-04</td>
</tr>
<tr>
<td>4</td>
<td>6.53E-08</td>
<td>6.53E-04</td>
</tr>
<tr>
<td>5</td>
<td>1.14E-07</td>
<td>1.14E-03</td>
</tr>
<tr>
<td>6</td>
<td>1.33E-07</td>
<td>1.33E-03</td>
</tr>
<tr>
<td>7</td>
<td>1.30E-07</td>
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<tr>
<td>8</td>
<td>1.28E-07</td>
<td>1.28E-03</td>
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<tr>
<td>9</td>
<td>1.19E-07</td>
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<td>10</td>
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<td>11</td>
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<td>14</td>
<td>1.33E-08</td>
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</tr>
<tr>
<td>15</td>
<td>8.15E-09</td>
<td>8.15E-05</td>
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<td>16</td>
<td>5.63E-09</td>
<td>5.63E-05</td>
</tr>
<tr>
<td>17</td>
<td>1.27E-09</td>
<td>1.27E-05</td>
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</tbody>
</table>

### Diagram: Photon Flux vs. Position

- X-axis: Position
- Y-axis: Photon Flux (Einstein/m²s)
## Reactor measurements

<table>
<thead>
<tr>
<th>Position</th>
<th>Photon Flux</th>
<th>Photon Flux</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
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<td>9.36E-09</td>
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<td>2</td>
<td>1.45E-08</td>
<td>1.45E-04</td>
<td></td>
</tr>
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<td>3</td>
<td>3.67E-08</td>
<td>3.67E-04</td>
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</tr>
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<td>1.30E-08</td>
<td>1.30E-04</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>9.55E-09</td>
<td>9.55E-05</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>8.08E-09</td>
<td>8.08E-05</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>4.33E-09</td>
<td>4.33E-05</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>4.22E-09</td>
<td>4.22E-05</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>4.59E-09</td>
<td>4.59E-05</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>6.27E-09</td>
<td>6.27E-05</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>7.25E-09</td>
<td>7.25E-05</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 8: Immersion-well reactor dimensions.
APPENDIX 9: Detailed set-up for MB photo-oxidation.
APPENDIX 10: Dye concentration by the Beer-Lambert law.

\[ A = \alpha \cdot l \cdot c \]

with

\[ A = \log_{10} \left( \frac{I_0}{I_1} \right) \]

\[ \alpha = \frac{4 \cdot \pi \cdot k}{\lambda} \]

\[ c = \frac{A}{\alpha \cdot l} \]

\[ c = \log_{10} \left( \frac{I_0}{I_1} \right) \cdot \frac{4 \cdot \pi \cdot k \cdot l}{\lambda} \]
APPENDIX 11: Nitrogen physisorption and ammonia-TPD analysis.

### Analytical Report

**Client:** A. Greidanus  
**Serial number:** 050125  
**Concerning:** Determination of the porous properties and surface acidity of three titanium dioxides by volumetric N\(_2\) physisorption at 77 K and NH\(_3\)-TPD.

### Introduction

Prior to the N\(_2\) adsorption and desorption measurements, the samples were dried in vacuum at 300°C in order to remove present moisture and other volatile components (this sample weight is used in the calculations). After the pre-treatment the isotherms were measured at 77 K on the Quantachrome Autosorb-6B. The isotherm provides information on the specific surface area S\(_{BET}\), the pore volume, the pore size distribution and micropore contribution.

Followed by the N\(_2\)-physisorption measurement part of the dry sample has been used for temperature-programmed desorption of ammonia (NH\(_3\)-TPD) between 373 K and 773 K (10 K/min). For NH\(_3\)-TPD the sample was in-situ treated up to 773 K to additionally remove volatile components that might negatively influence the measurement. Prior to the TPD measurement the sample was three times saturated with ammonia gas at 373 K, and the desorption measurement was started when the baseline was stable again. NH\(_3\)-TPD measurements were carried out on a Micromeritics TPR/TPD 2900 with a Thermal Conductivity Detector and provide information on the total amount of acid sites and an indication of the acidity of the surface groups.

### N\(_2\) physisorption

The three samples all show a type IV isotherm, which is indicative for mesoporous materials. Characteristic for this type is the uptake of nitrogen at medium relative pressures (p/p\(_0\)) due to condensation in the present pores. For the samples with Hombicat titanium dioxide (pure and with gold) this condensation takes place in two steps, between 0.5 and 0.7 p/p\(_0\) and above 0.85 p/p\(_0\). The third sample with TiO\(_2\) from Degussa plus gold, the condensation takes place only above approximately 0.9 p/p\(_0\), which indicates that this sample has only pores with larger diameters.

The absence of a plateau at high relative pressures as observed with the three samples is also an indication the pores are present just outside the measurement range (>200 nm), however this uptake is not necessarily caused by intraparticle pores but might also be caused by surface roughness or interparticle porosity.

The samples show the following characteristics:

<table>
<thead>
<tr>
<th>Sample name</th>
<th>S(_{BET}) (m(^2)/g)</th>
<th>Total pore volume (cm(^3)/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2) (Hombicat) (calcined)</td>
<td>160 ± 4</td>
<td>0.37*</td>
<td>4.3 + 25</td>
</tr>
<tr>
<td>0.6% Au/TiO(_2) (Homb.) (calcined)</td>
<td>156 ± 5</td>
<td>0.38*</td>
<td>4.4 + 25</td>
</tr>
<tr>
<td>0.6% Au/TiO(_2) (Degussa) (calcined)</td>
<td>49 ± 2</td>
<td>0.40*</td>
<td>50</td>
</tr>
</tbody>
</table>

* The result must be interpreted carefully because the nitrogen is still adsorbing at high relative pressure where the pore volume is determined.

The observed porosity values are within the line of expectations in comparison to previous measurements on titanium dioxides from the same suppliers treated at 400°C.
As the isotherm already revealed is the Hombicat TiO$_2$ a mesoporous material with a relative narrow distribution around 4.3 nm. Additional porosity with this sample is also observed at the high end of these pores resulting in a broad distribution with a minor maximum at 25 nm.

The Hombicat sample impregnated with gold shows no significant difference in porosity in comparison to the bare sample. Also the overlay of the pore size distribution shows a comparable plot indicating that the gold is not blocking any pores and either homogeneously distributed in the pores or mainly located on the outer surface of the particles.

The Degussa sample (P25) impregnated with gold shows a lower surface area with a comparable pore volume as the result of the significant larger pores present in this material, which are distributed around 50 nm. Some minor contribution of pores is also observed with this sample below 3 nm, but the contribution in surface area is only approximately 5 m$^2$/g with a pore volume of 0.003 cm$^3$/g.

**Temperature programmed desorption of NH$_3$**

NH$_3$-TPD has been conducted between 373 K and 773 K (10 K/min) and the spectra are shown below as well as the amount desorbed NH$_3$, which is calculated from the total area below the curves. This amount of desorbed ammonia is correlated to the amount of acidic sites on the surface of the sample. The low starting temperature is chosen because Titanium is known to have weak acid sites in comparison to zeolites and since micropores are absent the contribution of ammonia physisorption (would overestimate acidity) is believed to be minimal. The maximum temperature of 773 K is the maximum temperature in the preparation of the sample and exceeding this temperature might influence the morphology of the sample.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Desorbed NH$_3$ (mmol/g)</th>
<th>NH$_3$ (µmol/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (Hombicat)</td>
<td>0.66</td>
<td>4.2</td>
</tr>
<tr>
<td>0.6% Au/TiO$_2$ (Hombicat, calc.)</td>
<td>0.62</td>
<td>4.0</td>
</tr>
<tr>
<td>0.6% Au/TiO$_2$ (Degussa, calc.)</td>
<td>0.27</td>
<td>5.5</td>
</tr>
</tbody>
</table>

The above results clearly show the significant lower desorption of NH$_3$ for the Degussa sample which points out the lower amount of acid sites with this sample. When the amount of ammonia is however corrected for the total surface area ($S_{BET}$), it shows that this value is approximately ¼ higher in comparison to the Hombicat samples. This observation might be an indication that the density of the surface acidity groups is higher for Degussa in comparison to the Hombicat samples.

The Hombicat samples with and without gold both show a very comparable desorption profile and almost an overlay in the curve. Integration of the graph shows however a 6% lower value for the sample with gold. Since the curves are very similar it is questionable whether this is the result of the precipitated gold on the surface blocking specific groups.

The sample shows the following characteristics:

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Total pore volume (cm$^3$/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0% Au/TiO$_2$ (calcined)</td>
<td>147 ± 4</td>
<td>0.36*</td>
<td>4.5 + 25 (Homb.)</td>
</tr>
<tr>
<td>TiO$_2$ (Hombicat) (calcined)</td>
<td>160 ± 4</td>
<td>0.37*</td>
<td>4.3 + 25</td>
</tr>
<tr>
<td>0.6% Au/TiO$_2$ (calcined)</td>
<td>156 ± 5</td>
<td>0.38*</td>
<td>4.4 + 25 (Hombi.)</td>
</tr>
</tbody>
</table>

* The result must be interpreted carefully because the nitrogen is still adsorbing at high relative pressure where the pore volume is determined.

The pore size distribution is bimodal and not significantly influenced by the gold present on the surface of the Hombicat titanium. The slight reduction in surface area with the amount of gold loading on the sample might be due to the dilution of the porous titanium with gold, indicating that the gold does not introduce nor reduce the porosity of TiO$_2$ significantly.
The desorption profile of the new sample is given in the above graph and is rather comparable to the other Hombicat samples. The observed difference in the amount desorbed NH$_3$ is at least an indication that the quantity of acidic surface groups reduces upon the loading of gold although the differences are within the variation of the analysis. Possibly however, this observed reduction in acidity is also the consequence of a dilution of the titanium.

The samples show the following characteristics:

### Sample name

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Desorbed NH$_3$ (mmol/g)</th>
<th>NH$_3$ (µmol/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0% Au/TiO$_2$ (H, calc.)</td>
<td>0.63</td>
<td>4.3</td>
</tr>
<tr>
<td>TiO$_2$ (H, calc.)</td>
<td>0.66</td>
<td>4.2</td>
</tr>
<tr>
<td>0.6% Au/TiO$_2$ (H, calc.)</td>
<td>0.62</td>
<td>4.0</td>
</tr>
</tbody>
</table>

* The result must be interpreted carefully because the nitrogen is still adsorbing at high relative pressure where the pore volume is determined.

It is clearly from the above results that the Hombikat sample is most porous followed by the sample from Merck. The samples from both Aldrich and P25 show barely any porosity and their surface area is likely located on the outside of the primary particles.

The Hombikat sample appears to show a bimodal pore size distribution but the pores distributed around < 2 nm are likely intra-particle pores (inside the primary particles) and pore distributed around 25 nm are expected to be inter-particle porosity (between the primary particles). The presence of gold on these samples is expected to have no significant influence on the porosity but since the results are expressed per gram sample, the dilution of the porous medium could have some effect.

### Sample name

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Desorbed NH$_3$ (mmol/g)</th>
<th>S$_{BET}$ (m$^2$/g)</th>
<th>NH$_3$ (µmol/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Au / TiO$_2$ (Hombikat)</td>
<td>0.88</td>
<td>317</td>
<td>2.8</td>
</tr>
</tbody>
</table>
The above results clearly show the correlation with the desorption amount of ammonia with the total surface area (S_{BET}). The Hombikat sample has the highest surface acidity, followed by P25. The samples from Merck and Aldrich have the lowest desorption of ammonia and corresponding surface acidity. The representation of the desorption amount per total surface area appears not to be a good quantity in this case, because it suggests the lowest activity for the Hombikat sample. What can be observed in the graph is that the Hombikat sample still shows desorption at 673K. To this end the desorption of a fresh sample has also been measured up to 823 K after pre-treating it up to 823 K as well. This sample indeed shows some desorption above 673 K, but the amount is minor. This sample treated up to 823 K is however not completely comparable to the Hombikat sample that has been treated up to 673 K because it shows a much lower desorption quantity in the overlaying region and also a lower overall desorption. This difference is likely caused by the fact that the pre-treatment at 823 K caused significant changes to the sample.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Desorption Amount</th>
<th>Total Surface Area</th>
<th>Surface Acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Au / TiO₂ (Aldrich)</td>
<td>0.06</td>
<td>11</td>
<td>5.5</td>
</tr>
<tr>
<td>1% Au / TiO₂ (P25)</td>
<td>0.19</td>
<td>49</td>
<td>3.8</td>
</tr>
<tr>
<td>1% Au / TiO₂ (Merck)</td>
<td>0.06</td>
<td>11</td>
<td>5.1</td>
</tr>
<tr>
<td>1% Au / TiO₂ (Hombikat-high temp)</td>
<td>0.60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 12: Pore distributions.

Figure 1: Pore distribution of chemical reduced and calcined catalysts.

Figure 2: Pore distribution of all chemical reduced catalysts.
APPENDIX 13: XRD Data

**Rutile**

Table 1: Intensity of XRD rutile peaks

<table>
<thead>
<tr>
<th>2theta</th>
<th>P25</th>
<th>Au P25</th>
<th>Au P25 0.6wt% calc</th>
<th>Hombikat calc</th>
<th>Hombikat, calc</th>
<th>Au Hombi</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.6</td>
<td>[110]</td>
<td>133</td>
<td>129</td>
<td>115</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>36.1</td>
<td>[101]</td>
<td>57</td>
<td>50</td>
<td>50</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>41.2</td>
<td>[111]</td>
<td>30</td>
<td>31</td>
<td>36</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>54.3</td>
<td>[211]</td>
<td>82</td>
<td>82</td>
<td>75</td>
<td>7</td>
<td>47</td>
</tr>
<tr>
<td>62.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAX (rutile)</td>
<td>133</td>
<td>129</td>
<td>115</td>
<td>7</td>
<td>47</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2theta</th>
<th>Au Hombi 0.6wt% calc</th>
<th>Au Hombi 2wt% calc</th>
<th>Merck</th>
<th>Au Merck</th>
<th>Aldrich</th>
<th>Au Aldrich</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.78</td>
<td>[110]</td>
<td>12</td>
<td>14</td>
<td>14</td>
<td>18</td>
<td>9</td>
</tr>
<tr>
<td>36.28</td>
<td>[101]</td>
<td>15</td>
<td>14</td>
<td>9</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>41.38</td>
<td>[111]</td>
<td>10</td>
<td>7</td>
<td>9</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>54.48</td>
<td>[211]</td>
<td>42</td>
<td>48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62.88</td>
<td></td>
<td></td>
<td></td>
<td>128</td>
<td>126</td>
<td>125</td>
</tr>
<tr>
<td>MAX (rutile)</td>
<td>42</td>
<td>48</td>
<td>128</td>
<td>126</td>
<td>125</td>
<td>126</td>
</tr>
</tbody>
</table>

**Anatase**

Table 2: Intensity of XRD anatase peaks

<table>
<thead>
<tr>
<th>2theta</th>
<th>P25</th>
<th>Au P25</th>
<th>Au P25 0.6wt% calc</th>
<th>Hombikat calc</th>
<th>Hombikat, calc</th>
<th>Au Hombi</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.4</td>
<td>[101]</td>
<td>443</td>
<td>428</td>
<td>427</td>
<td>198</td>
<td>316</td>
</tr>
<tr>
<td>37.9</td>
<td>[004]</td>
<td>92</td>
<td>90</td>
<td>98</td>
<td>45</td>
<td>65</td>
</tr>
<tr>
<td>48.2</td>
<td>[200]</td>
<td>113</td>
<td>122</td>
<td>111</td>
<td>59</td>
<td>85</td>
</tr>
<tr>
<td>53.8</td>
<td>[105]</td>
<td>89</td>
<td>69</td>
<td>75</td>
<td>38</td>
<td>51</td>
</tr>
<tr>
<td>55</td>
<td>[211]</td>
<td>82</td>
<td>78</td>
<td>64</td>
<td>53</td>
<td>54</td>
</tr>
<tr>
<td>MAX (anatase)</td>
<td>443</td>
<td>428</td>
<td>427</td>
<td>198</td>
<td>316</td>
<td>178</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2theta</th>
<th>Au Hombi 0.6wt% calc</th>
<th>Au Hombi 2wt% calc</th>
<th>Merck</th>
<th>Au Merck</th>
<th>Aldrich</th>
<th>Au Aldrich</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.58</td>
<td>[101]</td>
<td>304</td>
<td>305</td>
<td>1233</td>
<td>1194</td>
<td>1206</td>
</tr>
<tr>
<td>38.08</td>
<td>[004]</td>
<td>63</td>
<td>76</td>
<td>224</td>
<td>213</td>
<td>206</td>
</tr>
<tr>
<td>48.38</td>
<td>[200]</td>
<td>88</td>
<td>84</td>
<td>288</td>
<td>291</td>
<td>315</td>
</tr>
<tr>
<td>53.98</td>
<td>[105]</td>
<td>46</td>
<td>46</td>
<td>209</td>
<td>179</td>
<td>170</td>
</tr>
<tr>
<td>55.18</td>
<td>[211]</td>
<td>62</td>
<td>63</td>
<td>175</td>
<td>151</td>
<td>174</td>
</tr>
<tr>
<td>MAX (anatase)</td>
<td>304</td>
<td>305</td>
<td>1233</td>
<td>1194</td>
<td>1206</td>
<td>1065</td>
</tr>
</tbody>
</table>
Table 3: Fraction Anatase and Rutile phase for several catalysts, determined by XRD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rutile Intensity</th>
<th>Anatase Intensity</th>
<th>Wa</th>
<th>Wr</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>133</td>
<td>443</td>
<td>72,5%</td>
<td>27,5%</td>
</tr>
<tr>
<td>Au P25</td>
<td>129</td>
<td>428</td>
<td>72,4%</td>
<td>27,6%</td>
</tr>
<tr>
<td>Au P25 0.6wt% calc</td>
<td>115</td>
<td>427</td>
<td>74,6%</td>
<td>25,4%</td>
</tr>
<tr>
<td>Hombikat</td>
<td>0</td>
<td>198</td>
<td>100,0%</td>
<td>0,0%</td>
</tr>
<tr>
<td>Hombikat, calc</td>
<td>35</td>
<td>316</td>
<td>87,7%</td>
<td>12,3%</td>
</tr>
<tr>
<td>Au Hombi</td>
<td>0</td>
<td>178</td>
<td>100,0%</td>
<td>0,0%</td>
</tr>
<tr>
<td>Au Hombi 0.6wt% calc</td>
<td>42</td>
<td>297</td>
<td>84,8%</td>
<td>15,2%</td>
</tr>
<tr>
<td>Au Hombi 2wt% calc</td>
<td>48</td>
<td>268</td>
<td>81,5%</td>
<td>18,5%</td>
</tr>
<tr>
<td>Merck</td>
<td>128</td>
<td>1233</td>
<td>88,4%</td>
<td>11,6%</td>
</tr>
<tr>
<td>Au Merck</td>
<td>126</td>
<td>1194</td>
<td>88,2%</td>
<td>11,8%</td>
</tr>
<tr>
<td>Aldrich</td>
<td>125</td>
<td>1206</td>
<td>88,4%</td>
<td>11,6%</td>
</tr>
<tr>
<td>Au Aldrich</td>
<td>126</td>
<td>1065</td>
<td>87,0%</td>
<td>13,0%</td>
</tr>
</tbody>
</table>
APPENDIX 14: TGA data

Figure 73: Thermal gravimetric analysis of four different TiO$_2$-based catalysts, a. Degussa P25, b. Hombikat, c. Merck, d. Aldrich.

Table 1: Weight loss during TGA analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>end T °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Hombicat</td>
<td>4.04%</td>
</tr>
<tr>
<td>Au/Hombicat</td>
<td>3.82%</td>
</tr>
<tr>
<td>Merck</td>
<td>0.03%</td>
</tr>
<tr>
<td>Au/Merck</td>
<td>0.05%</td>
</tr>
<tr>
<td>P25</td>
<td>0.07%</td>
</tr>
<tr>
<td>Au/P25</td>
<td>0.33%</td>
</tr>
<tr>
<td>Aldrich</td>
<td>0.03%</td>
</tr>
<tr>
<td>Au/Aldrich</td>
<td>0.03%</td>
</tr>
</tbody>
</table>

Hombicat samples have a large decrease in weight during the TGA measurements (around 12wt% up till 600 °C).
APPENDIX 15: TPD-MS data

Figure 1: TPD-MS of Hombicat, 25° C to 600° C, heating ramp of 10° C/min.

Both figures shows that they loose much water and OH-groups compared to other components, like CO₂.
Gold deposition causes additional light absorbance at higher wavelengths for all TiO$_2$ supports; around 540 nm there is an obvious peak.
APPENDIX 17: Cyclohexane oxidation. Cyclohexanone development and photonic efficiency.

Figure 1: Cyclohexanone formation over calcined Hombicat and Au/Hombicat and corresponding photon efficiency.

Figure 2: Cyclohexanone formation over chemical reduced Hombicat and Au/Hombicat and corresponding photon efficiency.

Figure 3: Cyclohexanone formation over chemical reduced P25 and Au/P25 and corresponding photon efficiency.
Figure 4: Cyclohexanone formation over chemical reduced Merck and Au/Merck and corresponding photon efficiency.
APPENDIX 18: MB decomposition (duplo)

Figure 1: MB degradation profile for Hombicat and Au/Hombicat (duplo)

Figure 2: MB degradation profile for P25 and Au/P25 (duplo)

Figure 3: MB degradation profile for Au/Merck (duplo)

Figure 4: MB degradation profile for Aldrich and Au/Aldrich (duplo)

<table>
<thead>
<tr>
<th></th>
<th>$k$ (min$^{-1}$)</th>
<th>$t_{50% C_0}$ (min)</th>
<th>$t_{10% C_0}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hombicat</td>
<td>6.01E-03</td>
<td>179.6</td>
<td>219.9</td>
</tr>
<tr>
<td>Au/Homb</td>
<td>1.27E-02</td>
<td>65.4</td>
<td>181.0</td>
</tr>
<tr>
<td>P25</td>
<td>2.88E-02</td>
<td>26.8</td>
<td>95.9</td>
</tr>
<tr>
<td>Au/P25</td>
<td>1.84E-02</td>
<td>43.1</td>
<td>131.2</td>
</tr>
<tr>
<td>Au/Merck</td>
<td>3.26E-02</td>
<td>21.0</td>
<td>73.9</td>
</tr>
<tr>
<td>Aldrich</td>
<td>4.00E-02</td>
<td>13.3</td>
<td>219.9</td>
</tr>
<tr>
<td>Au/Aldr</td>
<td>1.33E-02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 19: Calculation of MB rate constant fluctuations due to temperature fluctuations.

Arrhenius Equation:

\[ k = A e^{\frac{-E_A}{RT}} \]

\[ \begin{align*}
E_A &= 36000 \text{ J/mol} \\
R &= 8.314 \text{ J/mol/K} \\
T_1 &= 303 \text{ K} \\
T_2 &= 308 \text{ K}
\end{align*} \]

\[ \frac{k_2}{k_1} = \frac{e^{\frac{-E_A}{RT_2}}}{e^{\frac{-E_A}{RT_1}}} = 1.26 \]

Rate fluctuates **20-30%** when the temperature fluctuates between 30 and 35 °C.
APPENDIX 20: Calculation of Weisz-Prater criterion for diffusion limitation.

\[
\ln \alpha = \frac{1302}{T} - 2.63
\]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>305 K</td>
</tr>
<tr>
<td>\alpha</td>
<td>5.15</td>
</tr>
</tbody>
</table>

\[
D_e = \frac{D_m \epsilon}{\tau} e^{-\frac{d_{molecular}}{d_{pore}}}
\]

<table>
<thead>
<tr>
<th>Dm</th>
<th>1.66E-10 m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>\epsilon/\tau</td>
<td>0.1</td>
</tr>
<tr>
<td>d_{molecular}</td>
<td>1.52 nm</td>
</tr>
<tr>
<td>d_{pore}</td>
<td>4 nm</td>
</tr>
<tr>
<td>De</td>
<td>2.346E-12 m²/s</td>
</tr>
</tbody>
</table>

To have NO diffusion limitation:

\[
\Phi = \frac{V k_{app} \cdot \rho_p \cdot d_p^2}{m_{cat} 36 \cdot D_e} < 0.15
\]

<table>
<thead>
<tr>
<th>k_{app}</th>
<th>2.75E-02 /min</th>
</tr>
</thead>
<tbody>
<tr>
<td>m_{cat}</td>
<td>50 mg</td>
</tr>
<tr>
<td>V</td>
<td>100 ml</td>
</tr>
<tr>
<td>\rho_p</td>
<td>2400 g/L</td>
</tr>
<tr>
<td>d_p</td>
<td>3.3 micro_m</td>
</tr>
<tr>
<td>Cs=Cb</td>
<td></td>
</tr>
</tbody>
</table>

\[
\Phi = 0.28
\]

Concluded: There is diffusion limitation.