TiO₂ based photocatalytic gas purification

the effects of co-catalysts and process conditions

Bindikt D. Fraters

**TiO₂ BASED PHOTOCATALYTIC
GAS PURIFICATION**

**THE EFFECTS OF CO-CATALYSTS AND PROCESS
CONDITIONS**

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1

GENERAL INTRODUCTION

1. Heterogenous Photocatalysis

1.1 Air purification and industrial air cleaning

Worldwide the importance of air quality on the political agenda is steadily increasing. Two most notorious examples of air pollution are the smog in cities in winter, or in wind-less periods. However poor outdoor air quality is not the only silent killer, resulting in huge economic losses. The quality of indoor air, where people spend up to 80% of their time, is in majority also poor, resulting in a large range of health related symptoms, like headaches, fatigue and asthma symptoms, all classified as the Sick Building Syndrome (SBS) [1, 2]. The potential savings by improving the indoor air quality are only in the US estimated to be between \$ 17 -43 billion. Improved health quality of the employees results additionally in higher productivity and motivation, inducing another potential benefit in the range of \$ 12- 125 billion [1].

The major cause of the SBS is a high concentration of volatile organic compounds (VOC's) in the indoor air. The sources of VOC's are diverse and diffuse. Important sources of VOC's are the building materials in the building itself, and from furniture [3]. Furthermore, other important sources of VOC's are for example cleaning detergents, and outdoor air. Currently most climate control systems are not able to remove or mineralize the VOC's [4].

Mitigation of the air pollution and cleaning of the air require therefore new technologies. Photocatalysis is one of the technologies which has the potential to become commercially feasible for air cleaning processes in the near future [2, 5, 6], taking into consideration the number of currently available patents [7]. However, practical indoor applications are currently limited, and in this chapter the challenges in improving photocatalysis will be discussed in more detail.

1.2 Basics of heterogeneous photocatalysis

In heterogeneous photocatalysis a solid semiconductor material is used to perform chemical reactions, stimulated by photons as energy source. A large range of semi-conductors is available to induce photocatalysis, while TiO_2 is seen as one of the most promising catalysts for practical application. This material is cheap and abundantly available, it is highly chemically stable, and safe to use [8]. However one of its major limitations is the large band gap of 3.2 eV, making it only active upon exposure to UV-light [9]. Furthermore the high recombination rate of electrons and holes [10], makes that photocatalytic reactions using TiO_2 have poor energy efficiencies. The electron (and hole) transfer steps are illustrated in Figure 1.

Figure 1: Schematic overview of the basic reaction steps occurring within a photocatalyst during reaction

The first step in a photocatalytic reaction is when photons with sufficient energy are absorbed by the photocatalyst, generating an electron and a hole, as shown in Figure 1. These electrons and holes can induce redox reactions of reactants A and D , when these adsorb on the catalyst surface, often via the formation of radicals as shown in equations 1 and 2.

The surface chemical reaction steps can be summarized in the following order:

1. Diffusion of the reactant from the bulk to the surface
2. Adsorption of reactant(s) on the surface
3. Absorption of photons and generation of electron hole pairs
4. Transfer of electrons and holes to the catalytic surface and to the adsorbed species
5. Reaction of adsorbed species to products
6. Desorption of products
7. Diffusion of products from surface to bulk

In Figure 1, steps 1 and 7, i.e. the diffusion of the products and reactants, are not shown. The adsorption and desorption of respectively the reactants (A/D) and products (A⁺/D⁺) in steps 2 and 6 are shown in Figure 1 by the arrows associated with A and D. After the electrons and holes are formed, as described by step 3, these electrons and holes have to reach the catalytic surface. In TiO₂, the mobility of electrons is high. The holes however only move slowly in comparison. Furthermore one of the important sources for recombination of electrons and holes is the presence of defects in the lattice. These defects act as traps for either the electrons or holes, ultimately resulting in recombination. In section 1.3 the opto-electronic properties of the catalysts, like light absorption and charge recombination, will be discussed in more detail. When the electrons finally reach the surface, they can react with the adsorbed species (step 5), followed by product desorption (step 6).

1.3 Other Applications of photocatalytic oxidation

Photocatalytic air purification is only one of the many different applications of photocatalysis which is being researched. Besides air purification, water cleaning [11, 12] is another important field of study. Photocatalysis has the

ability to eliminate a large range of organic compounds, like antibiotics, which are currently difficult to remove from sources for production of drinking water [13]. Furthermore, it can eliminate the current waste producing use of chemicals required for water cleaning [11]. More in depth information about the current challenges in water cleaning using photocatalysis can be found in the paper of Chong et al. [11].

One of the main advantages of using photocatalysis is the ability to operate reactions at room temperature, and this is especially relevant for selective oxidation reactions [14, 15]. Selective oxidation using photocatalysis potentially offers an alternative, safer and greener, route for the synthesis of valuable chemicals. In the paper of Palmisano et al. [16] an overview is provided on the selective oxidation of alkanes and alcohols. Besides for oxidation reactions, significant effort has also been spent on using photocatalysis for energy storage and synthesis reactions via respectively solar light water splitting [17], or CO₂ reduction to hydrocarbons [18, 19]. Application of photocatalysis for reduction is not only limited to CO₂, also the reduction of nitrogen compounds are among the options being investigated [16].

2. Problem Statement

2.1 Gas phase oxidation

Gas phase oxidation for indoor and industrial air purification is, based on the number of patents [7], one of the technologies closest to commercialization. However fundamental understanding of the chemistry for these advanced oxidation processes is often very limited. Whereas air purification would strongly benefit health by removing VOC's, a major risk is the possible formation of intermediates that could be released, which could actually be more harmful than the original species [2]. Improved understanding of the photocatalytic reaction mechanism of oxidation of substrates is therefore essential.

2.2 Co-catalysts

Currently, efficiencies of photocatalysts are limited, and the addition of noble metal co-catalysts is seen as one of the most promising solutions to improve the efficiency of electron hole separation. However in gas phase oxidation reactions, understanding of the effect of noble metal co-catalysts is limited. This is due to the use of many different reactants, reaction conditions, photocatalytic materials and co-catalysts. Thus, there is still a need for study of how morphology and composition of co-catalyst nanoparticles relate to the photocatalytic activity. Furthermore, also the understanding of the properties, like particle size of the photocatalysts, on effectiveness is limited, which is essential to develop better photocatalysts.

3. Background

As stated, currently the use of photocatalysis in gas phase applications is limited by low efficiencies and possible selectivity issues. The use of co-catalyst is seen as highly promising to solve these issues [20], and this requires more fundamental mechanistic understanding. The parameters influencing the photocatalytic reaction can be organized into three different themes, namely: surface chemistry, opto-electronic properties, and reaction conditions. Since noble metal nanoparticles are relevant to all these three themes, these themes will be discussed separately in the following.

3.1 Photocatalyst opto-electronic properties

Two major limitations currently exist with TiO_2 photocatalysts, which are related to the opto-electronic properties: 1) the large band gap [9, 21], and 2) the high recombination rate of electrons and holes [10]. Many researchers focus on finding solutions for these issues. To reduce the band gap, doping is mostly considered [9, 22]. However, doping of TiO_2 often results in an increase in concentration of trap sites, responsible for the

recombination of electrons and holes [2, 23]. Even without doping, recombination is already a significant problem [24].

A reduction in the recombination rate can be achieved by reduction of the number of trap sites within the photocatalyst. Annealing of the catalysts in general will increase the crystallinity, and in this way reduce the number of defects or traps [15]. A second method used to improve the separation of electrons and holes is the use of noble metal co-catalysts, like Pt [25, 26], Pd [27] and Au [25, 28]. By adding these metals in the form of nanoparticles to the photocatalyst, electrons will be transferred to the noble metal, whereas the holes remain in the photocatalyst. In addition, electron transfer to the reactant will occur catalytically over the metal surface [10].

On the surface of the photocatalyst itself, OH-groups are able to trap holes by forming hydroxyl radicals [10], while Ti^{4+} surface sites are able to trap electrons, reducing Ti^{4+} to Ti^{3+} [24, 25]. Consecutively these entities are able to transfer holes and electrons to the reactants. This will be further discussed in the following.

3.2 Photocatalyst surface chemistry

Like in thermal heterogeneous catalysis, the surface chemical properties strongly affect the reaction steps and mechanisms [20] and so, the activity and selectivity of the photocatalyst. As already described, the OH-groups are able to capture holes to form radicals, effective in oxidation reactions of organic compounds.

The OH-groups however also strongly influence the surface chemistry of the reaction in other ways. As explained in paragraph 1.2, two main reaction steps in the photocatalytic reaction are the adsorption of reactants and desorption of products. The reaction steps (4 and 5) for the transfer of electrons and holes are not limited to equation 1 and 2 and there are several reactions possible on, or near, the surface, as shown in equations 3-8. The presence of OH-groups makes the TiO_2 surface hydrophilic, and influences the adsorption and desorption of reactants and products [29].

Depending on the reactant, it might therefore interact directly with OH-groups, or indirectly with the surface [30]. In this way the adsorbed reactant can act also directly as a hole acceptor [20, 31].

The presence of OH-groups is seen as essential for photocatalytic reactions, as can be observed from its role in reactions 2 and 5-7 [20, 32, 33]. Next to the OH-groups, also oxygen plays an important role in photocatalytic oxidation reactions, as a radical formed by reduction, shown in reactions 1 and 3. However electrons and holes can potentially also recombine at the surface, as is shown in reaction 8. However, exact mechanisms are not always known, and further studies to improve the understanding of the effect of OH-group concentrations and of the chemical environment have to be performed [33].

The most commonly used reaction mechanism in heterogeneous photocatalysis is the Langmuir-Hinshelwood mechanism [23]. It assumes that both reactants adsorb on the surface before reacting. In the case of gas phase oxidation reactions, these will be a hydrocarbon and oxygen. One of the important parameters is then the number of adsorption sites, which is directly related to the surface area of the TiO_2 and thus the particle size [34]. In general it can be stated that the smaller the TiO_2 particles, the higher the number of reaction sites. Whether oxygen and the hydrocarbon adsorb on the same reaction sites and thus are in competition, is not well known [35].

3.3 Reaction conditions

Within the research to improve photocatalysis, a significant effort is spent on improving the photocatalyst properties. To measure the improvement, in general specific reaction conditions are selected, like dye degradation in aqueous conditions [36, 37], or specific hydrocarbons for gas phase reactions [14, 38, 39]. Often only one single reaction condition is selected. Depending on the properties of the catalysts, the behavior of the catalyst might be completely different under different conditions [40], due to changes in the rate limiting steps. This makes equal comparison of photocatalysts challenging.

By changing reaction conditions for the same catalyst it will become possible to obtain better fundamental understanding of the photocatalytic properties, and this will also help to obtain more general design rules for the structuring of specific photocatalytic processes.

The general equation for the reaction rate in photocatalytic oxidation is the following:

$$R = k [C]^a [O_2]^b [I]^c$$

So the reaction rate depends on the concentration of the hydrocarbon [C], oxygen [O₂], and the light intensity [I]. Furthermore, each of the individual parameters has its own order, which again depends on the regime the reaction is performed in. Variation of these parameters can result in more insight into the current limitations of the selected reaction conditions and how these limitations are linked to specific catalyst properties.

As already mentioned in 3.2, the hydrophilicity of the TiO₂ surface will influence the adsorption and desorption behavior of the reactants and products [29, 40]. Therefore the use of hydrocarbons with different molecular functionalities can help to get more insight into the charge transfer mechanisms. Ethanol for example will adsorb strongly to the surface and will form weaker adsorbed intermediates [41]. Propane on the other hand only weakly adsorbs to the surface due to its hydrophobicity,

while strongly binding intermediates might be formed, of which desorption is then the limiting step in such specific reactions [42].

Another interesting parameter is the humidity of the gas mixture [40, 41, 43]. Water on the one hand is seen as an essential part of the reaction, since it can replenish OH-groups and prevent deactivation [44] by forming OH-radicals [45], oxidizing surface contaminants. On the other hand water is also highly hydrophilic, and can therefore via competitive adsorption, block potential reaction sites, resulting in a reduced activity [20, 44, 46].

3.4 Co-catalysts

The addition of noble metal nanoparticles is seen as one of the most promising solutions to improve the activity of the photocatalyst [24]. Many reports are available in which the promoting effect of different noble metals was observed [20, 47, 48]. However also several reports exist in which no positive effect, or even a negative effect was observed, due to the addition of these nanoparticles [49, 50]. As the work done on gas phase oxidation is limited compared to liquid phase photocatalytic processes, so is the amount of research on the effect of noble metal nanoparticle addition on gas phase photocatalytic oxidation.

The most frequently advocated reason for the addition of noble metal particles to the photocatalyst is to improve the electron hole separation by capturing electrons [51]. Via different methods, like Time Resolved Microwave Conductivity (TRMC), it has been observed that the number of electrons in TiO_2 upon laser excitation is significantly reduced by the addition of the nanoparticles [28, 52]. In Figure 2, the general principle of electron hole separation is shown. The excited electron in the conduction band (CB) of the photocatalyst is at a higher energy level than the Fermi level of noble metal particles grown on the surface [10]. As a consequence the electrons will be driven to the noble metal, and cannot easily be transferred back, due to the higher energy level of the conduction band of the photocatalyst.

Figure 2: Schematic overview of electron hole separation within catalyst with conduction band (CB) and valence band (VB), using a noble metal co-catalyst

The addition of nanoparticles can, however, also have a second effect, for example catalyzing the transfer of the electron to the substrate accepting the electron. Due to its presence it can also alter the selectivity of a reaction by favoring certain reaction steps or pathways [27]. Furthermore, the presence of the nanoparticles can even result in a change of surface chemistry of the photocatalysts, since it was observed that the adsorption of reactants was significantly reduced by the presence of nanoparticles [53].

However, the true effect of the noble metal nanoparticle co-catalysts does not only depend on the nature of the selected noble metal. The loading [54-56] and particle size [57, 58] can also play a significant role on the observed activity. First of all, in most research done on optimizing the loading of nanoparticles, a range between 0.5-1% is reported [48, 59, 60]. The reasons given in literature for the observed optimum in loading, and negative effect at higher loading are diverse. Both in the work of Li [56], and Sun [61] it is speculated that at higher loadings the beneficial effect of Pt cannot be further increased, and Pt starts to play a role in increasing recombination rates of electrons and holes. Another explanation was given by Chen [62], who argued that Pt increases electron hole separation, while also reducing the number of active sites for the adsorption of the organic compound, limiting the reaction rate at higher Pt loadings. Regarding the effect of

particles size, in a number of studies it was seen that smaller noble metal nanoparticles resulted in a more active photocatalyst [53, 58, 63].

Not only can the presence of nanoparticles influence the surface properties of the photocatalyst, also the chemicals used for synthesis and deposition of the co-catalyst can affect the surface. In several cases it is reported that the number of OH-groups was reduced by co-catalyst addition[64], which was used to explain a lower observed activity.

Since noble metals often have different properties, combining different metals in an alloy can result in some remarkable phenomena [65]. However, there are only few synthesis procedures for alloys, if simultaneous control of the particle size is desired [66].

4. Aims and Thesis Outline

4.1 Aims

The main focus of this thesis will be on improving the understanding of the effects of co-catalysts and their properties on the activity and selectivity in gas phase photocatalytic oxidation reactions. To be able to define these effects accurately, it is first required to improve the understanding of the behavior of photocatalysts under different reaction conditions.

Besides the analysis of effects of the co-catalyst, synthesized by wet-chemical methods and deposited on commercial TiO₂, the third aim was to develop a preparation route for model type catalysts. These types of catalysts and co-catalysts should be well defined and structured, and also made via methods that will not introduce contamination or surface alteration of the TiO₂ substrate.

4.2 Thesis Outline

The use of photocatalysis for air purification is seen as highly promising, though as already described, still many fundamental questions are yet to be answered. In this thesis different steps will be taken to improve the fundamental understanding of the mechanisms occurring in photocatalytic gas phase oxidation of hydrocarbons. First, in **Chapter 2** some of the most important equipment used in this thesis will be explained in more detail.

In **Chapter 3** the focus will be on the development of a well-defined thin layer of TiO_2 photocatalysts. For the synthesis of these layers, supersonic cluster beam deposition (SCBD) was used. This technique allows the growth of layers with different particle and crystal sizes, and also the type of crystal depending on the annealing conditions during or after deposition. Besides the control over the coating properties, the use of this method also enables the possibility of using high concentrations of doping in future studies.

To optimize research on the model catalysts, it is, however, first required to improve understanding of the reaction environment on the catalyst performance. The focus is therefore on the use of the commercial catalyst Hombikat in **Chapter 4**. By using different annealing temperatures, it is possible to alter the number of OH-groups on the surface and also the crystallinity. In this chapter it is studied how the use of different reaction conditions in relation to the surface chemical properties influences the observed activity and selectivity in propane oxidation. Based on these relations it was possible to obtain more insight into the different limitations that are present during photocatalytic oxidation.

The use of noble metal co-catalysts nanoparticles is seen as one of the most promising ways to improve the photocatalytic performance by electron hole separation. The addition of Pt co-catalyst nanoparticles in **Chapter 5** adds a completely new dimension to the understanding of this promoting effect of co-catalysts. In this chapter two reactants with different molecular functionalities are compared in the oxidation reaction over both TiO_2 and Pt- TiO_2 . It was found that Pt changes surface selectivity of propane, and gas phase product selectivity in ethanol oxidation.

In **Chapter 6** the effect of the Pt co-catalyst particle size is described. Two different Pt nanoparticle size ranges were synthesized and loaded onto Hombikat annealed at 600 °C. After analysis, the samples were annealed at 300 °C and again after analysis, annealed at 500 °C. This annealing procedure resulted in an increase of the particle size and in this way the effect of 6 different Pt co-catalyst particle sizes on the photocatalytic activity could be studied. This study not only revealed a relation between the Pt particle size and the activity, it also resulted in some more fundamental understanding of the physical properties of TiO₂ interacting with Pt nanoparticles.

The currently most used synthesis methods are wet-chemical synthesis methods and they have two limitations. First of all, these methods are most suited for powders, while changes in surface composition of the photocatalyst by the deposition of the co-catalysts cannot be fully excluded. Therefore in **Chapter 7**, a spark generator setup is used for the gas phase synthesis of nanoparticles, and deposition of Au co-catalyst nanoparticles onto some of the coatings synthesized as described in Chapter 3, was achieved. Furthermore, especially for Au, it is known that the synthesis method can have a significant effect on the observed promoting effect of the nanoparticles in photocatalytic reactions. By excluding possible contaminations, in this way a more fundamental study of the mechanistic aspects should become possible. Both the deposition of pure metals and alloys are studied in this chapter and the results are briefly discussed.

In **Chapter 8** the most important results in this thesis are discussed in the broader picture of photocatalytic gas phase oxidation and an outlook is given on future work, both considering the fundamental aspects, as the steps to take towards a system suitable for commercial application in air purification.

5. References

- [1] W.J. Fisk, A.H. Rosenfeld, Estimates of Improved Productivity and Health from Better Indoor Environments, *Indoor Air*, 7 (1997) 158-172.
- [2] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, Photocatalytic purification of volatile organic compounds in indoor air: A literature review, *Atmos. Environ.*, 43 (2009) 2229-2246.
- [3] S. Wang, H.M. Ang, M.O. Tade, Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art, *Environ. Int.*, 33 (2007) 694-705.
- [4] R. Sharmin, M.B. Ray, Application of ultraviolet light-emitting diode photocatalysis to remove volatile organic compounds from indoor air, *J. Air Waste Manage. Assoc.*, 62 (2012) 1032-1039.
- [5] N.R. Neti, G.R. Parmar, S. Bakardjieva, J. Subrt, Thick film titania on glass supports for vapour phase photocatalytic degradation of toluene, acetone, and ethanol, *Chem. Eng. J.*, 163 (2010) 219-229.
- [6] J. Peral, X. Domènech, D.F. Ollis, Heterogeneous Photocatalysis for Purification, Decontamination and Deodorization of Air, *J. Chem. Technol. Biotechnol.*, 70 (1997) 117-140.
- [7] Y. Paz, Application of TiO₂ photocatalysis for air treatment: Patents' overview, *Appl. Catal., B*, 99 (2010) 448-460.
- [8] K. Nakata, A. Fujishima, TiO₂ photocatalysis: Design and applications, *J. Photochem. Photobiol., C*, 13 (2012) 169-189.
- [9] M.V. Dozzi, E. Selli, Doping TiO₂ with p-block elements: Effects on photocatalytic activity, *J. Photochem. Photobiol., C*, 14 (2013) 13-28.
- [10] H.H. Mohamed, D.W. Bahnemann, The role of electron transfer in photocatalysis: Fact and fictions, *Appl. Catal., B*, 128 (2012) 91-104.
- [11] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: A review, *Water Res.*, 44 (2010) 2997-3027.
- [12] Z. Xiong, J. Ma, W.J. Ng, T.D. Waite, X.S. Zhao, Silver-modified mesoporous TiO₂ photocatalyst for water purification, *Water Res.*, 45 (2011) 2095-2103.

- [13] D. Kanakaraju, B. Glass, M. Oelgemöller, Titanium dioxide photocatalysis for pharmaceutical wastewater treatment, *Environ. Chem. Lett.*, 12 (2014) 27-47.
- [14] J.J. Murcia, M.C. Hidalgo, J.A. Navío, V. Vaiano, P. Ciambelli, D. Sannino, Ethanol partial photooxidation on Pt/TiO₂ catalysts as green route for acetaldehyde synthesis, *Catal. Today*, 196 (2012) 101-109.
- [15] J.T. Carneiro, A.R. Almeida, J.A. Moulijn, G. Mul, Cyclohexane selective photocatalytic oxidation by anatase TiO₂: influence of particle size and crystallinity, *Phys. Chem. Chem. Phys.*, 12 (2010) 2744-2750.
- [16] G. Palmisano, E. Garcia-Lopez, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro, L. Palmisano, Advances in selective conversions by heterogeneous photocatalysis, *Chem. Commun.*, 46 (2010) 7074-7089.
- [17] R.M. Navarro Yerga, M.C. Álvarez Galván, F. del Valle, J.A. Villoria de la Mano, J.L.G. Fierro, Water Splitting on Semiconductor Catalysts under Visible-Light Irradiation, *ChemSusChem*, 2 (2009) 471-485.
- [18] O.K. Varghese, M. Paulose, T.J. LaTempa, C.A. Grimes, High-rate solar photocatalytic conversion of CO₂ and water vapor to hydrocarbon fuels, *Nano Lett.*, 9 (2009) 731-737.
- [19] C.-C. Yang, J. Vernimmen, V. Meynen, P. Cool, G. Mul, Mechanistic study of hydrocarbon formation in photocatalytic CO₂ reduction over Ti-SBA-15, *J. Catal.*, 284 (2011) 1-8.
- [20] M.A. Henderson, A surface science perspective on photocatalysis, *Surf. Sci. Rep.*, 66 (2011) 185-297.
- [21] A. Sclafani, J.-M. Herrmann, Influence of metallic silver and of platinum-silver bimetallic deposits on the photocatalytic activity of titania (anatase and rutile) in organic and aqueous media, *J. Photochem. Photobiol., A*, 113 (1998) 181-188.
- [22] E. Barborini, A.M. Conti, I. Kholmanov, P. Piseri, A. Podestà, P. Milani, C. Cepek, O. Sakho, R. Macovez, M. Sancrotti, Nanostructured TiO₂ Films with 2 eV Optical Gap, *Adv. Mater.*, 17 (2005) 1842-1846.

- [23] J.-M. Herrmann, Fundamentals and misconceptions in photocatalysis, *J. Photochem. Photobiol., A*, 216 (2010) 85-93.
- [24] L. Zhang, H.H. Mohamed, R. Dillert, D. Bahnemann, Kinetics and mechanisms of charge transfer processes in photocatalytic systems: A review, *J. Photochem. Photobiol., C*, 13 (2012) 263-276.
- [25] A. Naldoni, M. D'Arienzo, M. Altomare, M. Marelli, R. Scotti, F. Morazzoni, E. Selli, V. Dal Santo, Pt and Au/TiO₂ photocatalysts for methanol reforming: Role of metal nanoparticles in tuning charge trapping properties and photoefficiency, *Appl. Catal., B*, 130-131 (2013) 239-248.
- [26] K.L. Miller, C.W. Lee, J.L. Falconer, J.W. Medlin, Effect of water on formic acid photocatalytic decomposition on TiO₂ and Pt/TiO₂, *J. Catal.*, 275 (2010) 294-299.
- [27] R. Su, R. Tiruvalam, Q. He, N. Dimitratos, L. Kesavan, C. Hammond, J.A. Lopez-Sanchez, R. Bechstein, C.J. Kiely, G.J. Hutchings, F. Besenbacher, Promotion of Phenol Photodecomposition over TiO₂ Using Au, Pd, and Au-Pd Nanoparticles, *ACS Nano*, 6 (2012) 6284-6292.
- [28] J.T. Carneiro, T.J. Savenije, G. Mul, Experimental evidence for electron localization on Au upon photo-activation of Au/anatase catalysts, *Phys. Chem. Chem. Phys.*, 11 (2009) 2708-2714.
- [29] M.E. Zorn, S.O. Hay, M.A. Anderson, Effect of molecular functionality on the photocatalytic oxidation of gas-phase mixtures, *Appl. Catal., B*, 99 (2010) 420-427.
- [30] J.J. Murcia, M.C. Hidalgo, J.A. Navío, J. Araña, J.M. Doña-Rodríguez, In situ FT-IR study of the adsorption and photocatalytic oxidation of ethanol over sulfated and metallized TiO₂, *Appl. Catal., B*, 142-143 (2013) 205-213.
- [31] G.L. Chiarello, D. Ferri, E. Selli, Effect of the CH₃OH/H₂O ratio on the mechanism of the gas-phase photocatalytic reforming of methanol on noble metal-modified TiO₂, *J. Catal.*, 280 (2011) 168-177.
- [32] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, Photocatalytic oxidation of gaseous toluene on anatase TiO₂ catalyst: mechanistic aspects and FT-IR investigation, *Appl. Catal., B*, 20 (1999) 15-27.

- [33] A. Di Paola, M. Bellardita, L. Palmisano, Z. Barbieriková, V. Brezová, Influence of crystallinity and OH surface density on the photocatalytic activity of TiO₂ powders, *J. Photochem. Photobiol., A*, 273 (2014) 59-67.
- [34] M. Ouzzine, M.A. Lillo-Ródenas, A. Linares-Solano, Photocatalytic oxidation of propene in gas phase at low concentration by optimized TiO₂ nanoparticles, *Appl. Catal., B*, 134–135 (2013) 333-343.
- [35] A.K. Boulamanti, C.J. Philippopoulos, Photocatalytic degradation of methyl tert-butyl ether in the gas-phase: A kinetic study, *J. Hazard. Mater.*, 160 (2008) 83-87.
- [36] J. Sá, M. Fernández-García, J.A. Anderson, Photoformed electron transfer from TiO₂ to metal clusters, *Catal. Commun.*, 9 (2008) 1991-1995.
- [37] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, Toward a Physically Sound Structure–Activity Relationship of TiO₂-Based Photocatalysts, *J. Phys. Chem. C*, 114 (2009) 327-332.
- [38] S.W. Verbruggen, K. Masschaele, E. Moortgat, T.E. Korany, B. Hauchecorne, J.A. Martens, S. Lenaerts, Factors driving the activity of commercial titanium dioxide powders towards gas phase photocatalytic oxidation of acetaldehyde, *Catal. Sci. Technol.*, 2 (2012) 2311-2318.
- [39] S.W. Verbruggen, S. Ribbens, T. Tytgat, B. Hauchecorne, M. Smits, V. Meynen, P. Cool, J.A. Martens, S. Lenaerts, The benefit of glass bead supports for efficient gas phase photocatalysis: Case study of a commercial and a synthesised photocatalyst, *Chem. Eng. J.*, 174 (2011) 318-325.
- [40] C.A. Korologos, C.J. Philippopoulos, S.G. Pouloupoulos, The effect of water presence on the photocatalytic oxidation of benzene, toluene, ethylbenzene and m-xylene in the gas-phase, *Atmos. Environ.*, 45 (2011) 7089-7095.
- [41] M. Takeuchi, J. Deguchi, S. Sakai, M. Anpo, Effect of H₂O vapor addition on the photocatalytic oxidation of ethanol, acetaldehyde and acetic acid in the gas phase on TiO₂ semiconductor powders, *Appl. Catal., B*, 96 (2010) 218-223.

- [42] T. van der Meulen, A. Mattson, L. Österlund, A comparative study of the photocatalytic oxidation of propane on anatase, rutile, and mixed-phase anatase–rutile TiO₂ nanoparticles: Role of surface intermediates, *J. Catal.*, 251 (2007) 131-144.
- [43] J.M. Coronado, M.E. Zorn, I. Tejedor-Tejedor, M.A. Anderson, Photocatalytic oxidation of ketones in the gas phase over TiO₂ thin films: a kinetic study on the influence of water vapor, *Appl. Catal., B*, 43 (2003) 329-344.
- [44] G.B. Raupp, C.T. Junio, Photocatalytic oxidation of oxygenated air toxics, *Appl. Surf. Sci.*, 72 (1993) 321-327.
- [45] M.M. Ameen, G.B. Raupp, Reversible Catalyst Deactivation in the Photocatalytic Oxidation of Diluteo-Xylene in Air, *J. Catal.*, 184 (1999) 112-122.
- [46] A.A. Assadi, A. Bouzaza, D. Wolbert, Photocatalytic oxidation of trimethylamine and isovaleraldehyde in an annular reactor: Influence of the mass transfer and the relative humidity, *J. Photochem. Photobiol., A*, 236 (2012) 61-69.
- [47] J.J. Murcia, M.C. Hidalgo, J.A. Navío, J. Araña, J.M. Doña-Rodríguez, Correlation study between photo-degradation and surface adsorption properties of phenol and methyl orange on TiO₂ Vs platinum-supported TiO₂, *Appl. Catal., B*, 150–151 (2014) 107-115.
- [48] S. Oros-Ruiz, J.A. Pedraza-Avella, C. Guzmán, M. Quintana, E. Moctezuma, G. del Angel, R. Gómez, E. Pérez, Effect of Gold Particle Size and Deposition Method on the Photodegradation of 4-Chlorophenol by Au/TiO₂, *Top. Catal.*, 54 (2011) 519-526.
- [49] J.J. Murcia, M.C. Hidalgo, J.A. Navío, V. Vaiano, D. Sannino, P. Ciambelli, Cyclohexane photocatalytic oxidation on Pt/TiO₂ catalysts, *Catal. Today*, 209 (2013) 164-169.
- [50] T. Sano, N. Negishi, K. Uchino, J. Tanaka, S. Matsuzawa, K. Takeuchi, Photocatalytic degradation of gaseous acetaldehyde on TiO₂ with photodeposited metals and metal oxides, *J. Photochem. Photobiol., A*, 160 (2003) 93-98.
- [51] C.A. Emilio, M.I. Litter, M. Kunst, M. Bouchard, C. Colbeau-Justin, Phenol Photodegradation on Platinized-TiO₂ Photocatalysts Related to Charge-Carrier Dynamics, *Langmuir*, 22 (2006) 3606-3613.

- [52] J.M. Warman, d.H. Matthijs P, P. Pierre, K. Theodorus P.M, v.d.Z.-A. Etty A, M. Adri, C. Ronald, Electronic processes in semiconductor materials studied by nanosecond time-resolved microwave conductivity—III. Al₂O₃, MgO and TiO₂ powders, *Radiat. Phys. Chem.*, 37 (1991) 433-442.
- [53] V. Iliev, D. Tomova, L. Bilyarska, G. Tyuliev, Influence of the size of gold nanoparticles deposited on TiO₂ upon the photocatalytic destruction of oxalic acid, *J. Mol. Catal. A: Chem.*, 263 (2007) 32-38.
- [54] A. Orlov, D. Jefferson, N. Macleod, R. Lambert, Photocatalytic Properties of TiO₂ Modified with Gold Nanoparticles in the Degradation of 4-Chlorophenol in Aqueous Solution, *Catal Lett*, 92 (2004) 41-47.
- [55] A.V. Vorontsov, V.P. Dubovitskaya, Selectivity of photocatalytic oxidation of gaseous ethanol over pure and modified TiO₂, *J. Catal.*, 221 (2004) 102-109.
- [56] F.B. Li, X.Z. Li, The enhancement of photodegradation efficiency using Pt–TiO₂ catalyst, *Chemosphere*, 48 (2002) 1103-1111.
- [57] J.J. Murcia, J.A. Navío, M.C. Hidalgo, Insights towards the influence of Pt features on the photocatalytic activity improvement of TiO₂ by platinisation, *Appl. Catal., B*, 126 (2012) 76-85.
- [58] S. Zhao, G. Ramakrishnan, P. Shen, D. Su, A. Orlov, The first experimental demonstration of beneficial effects of sub-nanometer platinum particles for photocatalysis, *Chem. Eng. J.*, 217 (2013) 266-272.
- [59] D. Hufschmidt, D. Bahnemann, J.J. Testa, C.A. Emilio, M.I. Litter, Enhancement of the photocatalytic activity of various TiO₂ materials by platinisation, *J. Photochem. Photobiol., A*, 148 (2002) 223-231.
- [60] V. Iliev, D. Tomova, L. Bilyarska, A. Eliyas, L. Petrov, Photocatalytic properties of TiO₂ modified with platinum and silver nanoparticles in the degradation of oxalic acid in aqueous solution, *Appl. Catal., B*, 63 (2006) 266-271.
- [61] B. Sun, A.V. Vorontsov, P.G. Smirniotis, Role of Platinum Deposited on TiO₂ in Phenol Photocatalytic Oxidation, *Langmuir*, 19 (2003) 3151-3156.

- [62] T. Chen, Z. Feng, G. Wu, J. Shi, G. Ma, P. Ying, C. Li, Mechanistic Studies of Photocatalytic Reaction of Methanol for Hydrogen Production on Pt/TiO₂ by in situ Fourier Transform IR and Time-Resolved IR Spectroscopy, *J. Phys. Chem. C*, 111 (2007) 8005-8014.
- [63] A.A. Ismail, D.W. Bahnemann, Mesostructured Pt/TiO₂ Nanocomposites as Highly Active Photocatalysts for the Photooxidation of Dichloroacetic Acid, *J. Phys. Chem. C*, 115 (2011) 5784-5791.
- [64] J. Carneiro, C.-C. Yang, J. Moma, J. Moulijn, G. Mul, How Gold Deposition Affects Anatase Performance in the Photo-catalytic Oxidation of Cyclohexane, *Catal Lett*, 129 (2009) 12-19.
- [65] R. Su, R. Tiruvalam, A.J. Logsdail, Q. He, C.A. Downing, M.T. Jensen, N. Dimitratos, L. Kesavan, P.P. Wells, R. Bechstein, H.H. Jensen, S. Wendt, C.R.A. Catlow, C.J. Kiely, G.J. Hutchings, F. Besenbacher, Designer Titania-Supported Au–Pd Nanoparticles for Efficient Photocatalytic Hydrogen Production, *ACS Nano*, 8 (2014) 3490-3497.
- [66] J. Lu, K.-B. Low, Y. Lei, J.A. Libera, A. Nicholls, P.C. Stair, J.W. Elam, Toward atomically-precise synthesis of supported bimetallic nanoparticles using atomic layer deposition, *Nat. Commun.*, 5 (2014).

2

**PHOTOCATALYST PREPARATION AND
CHARACTERIZATION**

Abstract

Controlling the properties of the photocatalyst is essential to improve the understanding of individual properties. To reach this, two different pathways are chosen. First of all via supersonic cluster beam deposition (SCBD), thin and well defined coatings of TiO_2 were produced. Secondly a commercial catalyst, Hombikat was used, which was annealed at different temperatures to obtain the most active catalysts. The addition of co-catalyst particles was again done via two methods, first of all via a spark generator, enabling the synthesis of particles with a narrow size distribution and deposition on the SCBD coatings. The second method was a wet-chemical synthesis route, suited for powders and is described in the individual chapters. The photocatalysts were analyzed in a photocatalytic testing system, which was able to prepare tailored mixtures of gas and vapour phase composition. The other two parts of the system consisted of the top illuminated batch reactor and a gas chromatograph (GC) for the analysis of the product gas mixture.

1. Introduction

Within the field of photocatalytic research, there are currently two pathways to obtain an effective photocatalyst. 1) One uses commercial photocatalysts, like P25 [1, 2] and Hombikat [3, 4]. 2) To design the photocatalyst to meet more preferred properties, the other pathway is to synthesize the catalysts, either using a liquid phase sol gel based technique [1, 2, 4] or gas phase deposition techniques [5, 6]. To further tune the properties of the photocatalyst, further alteration is possible by calcination[3, 7] or doping [5, 8].

In this thesis both commercial catalysts, as well as gas phase synthesized TiO_2 is used as photocatalyst. Whereas in the individual chapters the general procedures are described, in this chapter the different photocatalytic preparation techniques will be explained, as well as the home made system that was built to perform all the measurements that resulted in the catalytic data presented in this work.

2. Photocatalyst preparation

2.1 Supersonic cluster beam deposition (SCBD)

For the synthesis of well-defined coatings of TiO_2 , supersonic cluster beam deposition (SCBD) is used. This is a gas phase synthesis method, which uses a plasma to ablate a Ti-rod. As is shown in Figure 1, the rod is placed in a chamber and connected to a cathode [9]. The chamber is under ultra-high vacuum. Helium gas at 50 bar is introduced with pulses via the pulsed valve, resulting in a supersonic gas due to the large pressure difference [10]. The plasma is formed by a pulsed voltage over the rod and the anode. The metal vapor is condensed and particles form. The supersonic beam containing the particles exits the primary chamber via the nozzle [11].

Figure 1: Schematic representation of pulsed microplasma source chamber creating a supersonic cluster beam, illustration from Wegner et al. [10].

In the next chamber a skimmer narrows down the particle size distribution of the cloud. After the skimmer in the deposition chamber the particles are deposited on a substrate [11]. A small concentration of oxygen is introduced in the high vacuum chamber to achieve the oxidation of the particles towards TiO_2 . The thickness of the layer can be adapted by the deposition time. The structure and the crystallinity of the layers can be optimized by either in situ annealing during deposition, or by ex-situ annealing in a Joules oven. The sample holder in the deposition chamber had the option to place Si-wafer supports into an electrical circuit. The Si-wafer can be heated by passing a current through it, with the temperature depending on this current.

2.2. Spark generator and particle size selection

To improve the photocatalytic efficiency, noble metal co-catalyst particles are often used, as explained in chapter 1. For the synthesis of these particles, wet-chemical synthesis methods are most commonly used [12]. Another method is a gas phase method, based on a spark generator [13]. The advantages of this method are that 1) it is ideal for deposition of coatings, with a narrow size distribution [14], 2) there is no contamination

of the photocatalysts by synthesis residues [15], and 3) it has the potential to produce well defined alloys[16, 17].

The spark generator setup, operated at room temperature and pressure is shown in Figure 2. An inert gas like He or N₂ is introduced into the reaction chamber between the anode and cathode of the desired metal. A capacitor parallel to the electrodes is charged by a high voltage. When the breakdown voltage is reached, the gas between the electrodes is ionized, resulting in a spark discharge. As a result, a small fraction of the electrode material is evaporated and then condenses into small primary particles under the influence of cooling, and dilution by the gas flow. After the formation of the primary particles, larger agglomerates can form [13].

Figure 2: Schematic overview of the spark generator setup including particle size selection in DMA and deposition in ECP.

To obtain particles within a narrow size distribution, a differential mobility analyzer (DMA) is used [13]. The DMA consists of an inner rod, which is either the anode or the cathode and the cylindrical housing. Due to the applied charge, particles are attracted to the center rod and the smaller the particle size the faster they will reach the center rod. There is an exit slit in the rod, through which only particles within a narrow size interval exit, resulting in a narrow size distribution. The particle size selection can be varied by the gas flow rate and the applied voltage between the rod and the housing. The particles leaving the DMA are either positively or negatively charged and are transferred to the electrostatic precipitator (ESP), where the particles are deposited on the support. A voltage is applied

between the support and the housing, and the corresponding electric field drives charged particles onto the support. This requires that the support exhibits some conductivity. As the deposition current is very small (e.g. 10^{-12} A), the resistance of the support (from the contact to the deposition area) may be as large as $10^{12} \Omega$ without any risk of altering the electric field. Care has to be taken in establishing the electric contact to the support. An aerosol electrometer (AEM) was installed at the exit to confirm that the particles were deposited.

2.3 Powder catalysts coating

Whereas both these systems offer significant advantages in the development of model catalyst systems, their application at larger scale is currently limited. Therefore, the second preparation method for photocatalysts is based on the use of commercial Hombikat, which is further optimized by annealing at 600°C [3]. The Pt nanoparticles were synthesized by a wet-chemical procedure as will be described in the individual chapters 5 and 6, and deposited on the powder. To test these catalysts, the powder was suspended in distilled water and drop casted on glass supports to form a homogeneous coating.

3. Photocatalytic testing

The study of the effect of the reaction conditions on the activity of different photocatalysts is an important aspect of this thesis. Therefore a photocatalytic reaction system is built, which is highly flexible. The system consists of three individual parts, integrated into one system. The main focus is on the analysis of oxidation reactions in the gas (and vapor) phase. The first part is therefore a gas distribution system to create tailored gas mixtures. The second part is a top illuminated batch reactor, in which the 'on glass' supported photocatalytic coatings can be mounted. The last part is the gas chromatograph (GC) to analyze the products in the gas phase, so that selectivity and activity of the catalysts can be determined.

3.1 Gas and vapor preparation

The gas distribution system consists of two parts. The first part are the direct gas connections to propane, oxygen, nitrogen and CO₂. The mass flow controllers make it possible to tailor gas mixtures to the desired composition. The second part of the system consists of two saturators connected to individual nitrogen mass flow controllers. The saturators enable the formation of gas mixtures containing organic vapors, and/or water.

3.2 Reactor system

The reactor for the photocatalytic testing is a 2 ml top illuminated reactor, in which the photocatalytic coating can be mounted at the bottom of the reactor as shown in Figure 3 (Left). As light source an UV-LED is used. The intensity of the light can be varied till a maximum of 8 or 25 mW/cm², for respectively the 375 and 365 nm LED (Roithner APG2C1-375-S (100 mW) and APGC1-365-E (135 mW)). In most studies the light intensity applied is not well described. In this thesis the light intensity can accurately be determined and regulated via the control panel using a voltage between 0-5 V. The relations between the applied control voltage and light intensity for both LED's is shown in Figure 3 (Right). Before the reaction is started the reactor is flushed for 20 minutes. During the reaction the reactor is closed and after the reaction almost the complete content of the reactor is flushed into the GC for analysis.

Figure 3: (Left) Schematic drawing of the top illuminated batch reactor (picture courtesy of Bart Zaalberg). (Right) Relation between light intensity and applied voltage in control panel.

3.3 GC- Analysis

The gas mixture for analysis can contain light gases as CO and CO₂, up to heavier compounds like ethanol and acetone. To ensure good separation within the column, a GC program was made which includes several temperature steps. The different products are analyzed by a flame ionization detector (FID). This analyzer is only able to detect hydrocarbon molecules. However, CO and CO₂ cannot be detected by FID, and therefore they are first converted to methane by a methanizer.

3.4 DRIFT-Analysis

Most data is obtained by gas phase analysis of the product gas mixture. However, this only provided information on the overall reaction mechanism. To obtain more in-depth information about the reaction mechanisms on the surface of the different photocatalysts, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used. The photocatalyst powder is placed into a three-window cell. Two windows are for the infrared (IR) beam and the diffused infrared, and the third window is used for the introduction of the UV-light into the cell. The obtained spectra provided information about the surface intermediates and species formed during the reaction. The details of the DRIFT analysis are discussed in chapter 5.

4. References

- [1] J.J. Murcia, M.C. Hidalgo, J.A. Navío, J. Araña, J.M. Doña-Rodríguez, In situ FT-IR study of the adsorption and photocatalytic oxidation of ethanol over sulfated and metallized TiO₂, *Appl. Catal., B*, 142–143 (2013) 205–213.
- [2] T. van der Meulen, A. Mattson, L. Österlund, A comparative study of the photocatalytic oxidation of propane on anatase, rutile, and mixed-phase anatase–rutile TiO₂ nanoparticles: Role of surface intermediates, *J. Catal.*, 251 (2007) 131–144.
- [3] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, Toward a Physically Sound Structure–Activity Relationship of TiO₂-Based Photocatalysts, *J. Phys. Chem. C*, 114 (2009) 327–332.
- [4] K. Chhor, J.F. Bocquet, C. Colbeau-Justin, Comparative studies of phenol and salicylic acid photocatalytic degradation: influence of adsorbed oxygen, *Mater. Chem. Phys.*, 86 (2004) 123–131.
- [5] M. Chiodi, C.P. Cheney, P. Vilmercati, E. Cavaliere, N. Mannella, H.H. Weitering, L. Gavioli, Enhanced Dopant Solubility and Visible-Light Absorption in Cr–N Codoped TiO₂ Nanoclusters, *J. Phys. Chem. C*, 116 (2011) 311–318.
- [6] F. Della Foglia, T. Losco, P. Piseri, P. Milani, E. Selli, Photocatalytic activity of nanostructured TiO₂ films produced by supersonic cluster beam deposition, *J. Nanopart. Res.*, 11 (2009) 1339–1348.
- [7] M. Ouzzine, M.A. Lillo-Ródenas, A. Linares-Solano, Photocatalytic oxidation of propene in gas phase at low concentration by optimized TiO₂ nanoparticles, *Appl. Catal., B*, 134–135 (2013) 333–343.
- [8] M.V. Dozzi, E. Selli, Doping TiO₂ with p-block elements: Effects on photocatalytic activity, *J. Photochem. Photobiol., C*, 14 (2013) 13–28.
- [9] E. Barborini, P. Piseri, P. Milani, A pulsed microplasma source of high intensity supersonic carbon cluster beams, *J. Phys. D: Appl. Phys.*, 32 (1999) L105.

- [10] K. Wegner, P. Piseri, H.V. Tafreshi, P. Milani, Cluster beam deposition: a tool for nanoscale science and technology, *J. Phys. D: Appl. Phys.*, 39 (2006) R439.
- [11] E. Barborini, G. Bongiorno, A. Forleo, L. Francioso, P. Milani, I.N. Kholmanov, P. Piseri, P. Siciliano, A.M. Taurino, S. Vinati, Thermal annealing effect on nanostructured TiO₂ microsenors by supersonic cluster beam deposition, *Sens. Actuators, B*, 111–112 (2005) 22–27.
- [12] A. Hugon, N.E. Kolli, C. Louis, Advances in the preparation of supported gold catalysts: Mechanism of deposition, simplification of the procedures and relevance of the elimination of chlorine, *J. Catal.*, 274 (2010) 239–250.
- [13] N.S. Tabrizi, M. Ullmann, V.A. Vons, U. Lafont, A. Schmidt-Ott, Generation of nanoparticles by spark discharge, *J. Nanopart. Res.*, 11 (2009) 315–332.
- [14] M.E. Messing, R. Westerström, B.O. Meuller, S. Blomberg, J. Gustafson, J.N. Andersen, E. Lundgren, R. van Rijn, O. Balmes, H. Bluhm, K. Deppert, Generation of Pd Model Catalyst Nanoparticles by Spark Discharge, *J. Phys. Chem. C*, 114 (2010) 9257–9263.
- [15] B.O. Meuller, M.E. Messing, D.L.J. Engberg, A.M. Jansson, L.I.M. Johansson, S.M. Norlén, N. Tureson, K. Deppert, Review of Spark Discharge Generators for Production of Nanoparticle Aerosols, *Aerosol Sci. Technol.*, 46 (2012) 1256–1270.
- [16] N.S. Tabrizi, Q. Xu, N.M. van der Pers, U. Lafont, A. Schmidt-Ott, Synthesis of mixed metallic nanoparticles by spark discharge, *J. Nanopart. Res.*, 11 (2009) 1209–1218.
- [17] N.S. Tabrizi, Q. Xu, N.M. van der Pers, A. Schmidt-Ott, Generation of mixed metallic nanoparticles from immiscible metals by spark discharge, *J. Nanopart. Res.*, 12 (2010) 247–259.

3

SYNTHESIS OF PHOTOCATALYTIC TiO₂ NANO- COATINGS BY SUPERSONIC CLUSTER BEAM DEPOSITION

This chapter is based on:

Fraters, B.D., Cavaliere, E., Mul, G., Gavioli, L., Synthesis of photocatalytic TiO₂ nano-coatings by supersonic cluster beam deposition, *Journal of Alloys and Compounds*, 615 (2014), pp. S467-S471

Abstract

In this chapter we report on the photocatalytic behavior in gas phase propane oxidation of well-defined TiO_2 nanoparticle (NP) coatings prepared via Supersonic Cluster Beam Deposition (SCBD) on Si-wafers and quartz substrates. The temperature dependent crystal phase of the coatings was analyzed by Raman spectroscopy, and the morphology by High Resolution-Scanning Electron Microscopy.

SCBD deposition in the presence of oxygen enables the in situ synthesis of TiO_2 layers of amorphous NPs at room temperature. Adapting the deposition temperature to 500 °C or 650 °C leads to Anatase crystals of variable size ranges, and layers showing significant porosity. At 800 °C mainly Rutile is formed. Post annealing by wafer heating of the amorphous NPs prepared at room temperature results in comparable temperature dependent phases and morphologies.

Photocatalytic activity in propane oxidation was dependent on the morphology of the samples: the activity decreases as a function of increasing particle size. The presence of water vapor in the propane feed generally increased the activity of the wafer-heated samples, suggesting OH groups are not profoundly present on SCBD synthesized layers. In addition, a remarkable effect of the substrate (Si or Quartz) was observed: strong interaction between Si and TiO_2 is largely detrimental for photocatalytic activity.

The consequences of these findings for the application of SCBD to synthesize samples for fundamental (spectroscopic) study of photocatalysis are discussed.

1. Introduction

The costs sustained worldwide for healthcare and cleaning of the environment caused by air and water pollution are huge, while the number of solutions to such problems currently available are limited [1,2]. A promising technology to mitigate the effects of pollution is the use of photocatalysis, a process that favors photon induced reaction of pollutants with the aid of a light sensitive catalyst, such as TiO₂ [3]. TiO₂ is cheap and abundant, chemically stable and an environmentally friendly photocatalyst [4]. Photo-activated TiO₂ has been evaluated in water [5,6] and air [7,8] cleaning applications, selective oxidation reactions [9,10], water splitting [11] and CO₂ reduction reactions [12,13].

In practice, TiO₂-based photocatalytic applications are scarce. The large band gap (3.2 eV) of Anatase (the most active TiO₂ crystal phase) [14], allowing only UV photons ($\lambda < 380$ nm) to produce electron-hole pairs and stimulate redox processes on the catalyst surface, limit the efficiency of solar light utilization [15]. Furthermore, the majority of photon induced electron-hole pairs recombine, rendering them not available to stimulate surface redox processes [16].

Different solutions have been proposed to resolve the above issues, including (i) TiO₂ doping [17-19], to improve visible light absorption of the photocatalyst, (ii) crystal phase and morphology optimization to enhance lifetimes of photoexcited states and (iii) addition of metal nanoparticles (NP's) to enhance electron transfer rates [20,21]. Whereas many studies have been reported on the above indicated aspects, the relationship between TiO₂ morphology and efficiency in photocatalysis is still not completely understood. In addition, the outcome of modification by metal nanoparticles is difficult to predict [22], since positive as well as negative effects on the photocatalytic activity have been reported.

To further analyze the effect of Anatase morphology on performance, in particular in applications involving coatings, it is a requirement to synthesize catalysts with well-defined composition, size and morphology. This can potentially be achieved by wet chemical synthesis [16], [23] and

[24], or by supersonic cluster beam deposition (SCBD) [17], [19] and [25]. When supported on Si, these well-defined layers can be analyzed by attenuated total reflectance (ATR) infrared spectroscopy [26], with the ability to provide in depth insight in the mechanism of reactions occurring on photocatalytically active surfaces [27] and [28]. While wet chemical procedures have been assessed to produce catalyst layers on ATR crystals, SCBD based synthesis of TiO_2 on Si has not.

In this chapter we will report on the structure of TiO_2 coatings on Si substrates when synthesized via SCBD [25] and [29]. Crystal size and phase of the coatings will be demonstrated to be affected by the value of the elevated synthesis temperature, either applied during, or after layer deposition. The photocatalytic efficacy of Si supported layers will be compared with quartz supported layers. The substrate (Si or quartz) and morphology of the samples will be demonstrated to significantly affect the photocatalytic rates of propane oxidation to CO_2 .

2. Experimental set-up

2.1 Synthesis of TiO_2 thin coating

Nanostructured titanium oxide layers (the thickness can be tuned in the 10 nm to 1 μm range according to the experimental needs) were synthesized in high vacuum (base pressure 1×10^{-6} mbar) conditions by SCBD, using a pulsed microplasma cluster source with He as a carrier gas [30], [31] and [32]. Oxygen atmosphere was introduced in the cluster deposition chamber through a leak valve, leading to a constant pressure of 10^{-2} mbar during deposition. The source produces a beam of nanoclusters (diameters in the range of 2–10 nm) [30], [31] and [32], thus allowing growth of a highly porous thin layer [19], [31] and [32]. The nominal deposition rate was measured by a quartz microbalance. The typical growth of the layer thickness was 200 nm/h. The applied deposition time was 2 h. A Si(1 1 1)-wafer pre-coated with a thin (around 200 nm) W-layer obtained by magnetron sputtering in high vacuum was used as substrate, the presence

of the W-layer needed to prevent formation of titanium silicide during the deposition of the Ti-clusters [32]. The temperature of the substrate was varied between 500 and 800 °C during deposition. The temperature of the wafer was measured by a Raytech infrared pyrometer. In the case of post-annealing, the samples were synthesized at room temperature and subsequently the wafer was electrically heated in direct contact with air. Alternatively, three samples were synthesized by SCBD at room temperature and 10⁻² mbar O₂ pressure, and annealed for two hours in a Joules oven (Carbolite CWF 1100) at 500, 650 and 800 °C (ramp rate 10 K min⁻¹), respectively. This procedure was also applied to synthesize oxide nanoclusters on quartz glass.

A sample of commercial Hombikat UV100 (Sachtleben), which consists of 100% Anatase TiO₂, was annealed at 600 °C for 2 h (heating rate 10 K min⁻¹) in a Carbolite oven to obtain powder with high photocatalytic activity [33]. The obtained material was suspended in distilled water and treated in an ultrasonic bath (VWR Ultrasonic cleaner) for 30 min. The suspension was dropped on quartz substrate, and dried in a vacuum desiccator containing silica gel, resulting in 1 mg catalyst per coated sample. The sample was evaluated for photocatalytic activity without any further thermal treatment.

2.2 Raman & HR-SEM

The crystal phase of the coatings was analyzed using a Renishaw RL633 Raman Spectrometer, equipped with a He–Ne laser emitting at 633 nm. The light was filtered using a 1800 lines/mm grating. Spectra were taken at a power of 1.4 mW (10% of laser power) and using a 100× objective lens.

The morphology of the samples was examined by a FEI Sirion High Resolution-Scanning Electron Microscope (HR-SEM).

2.3 Photocatalytic activity

The photocatalytic activity of the samples was analyzed in gas phase propane oxidation as follows. A gas mixture of 0.5% propane, 19.5% O₂ and 80% N₂ was led into a 2 ml top illumination reactor. The prepared sample on the quartz or Si-wafer pieces were placed at the bottom of the reactor. The reactor was illuminated for 60 min with a 375 nm UV-LED, with an intensity of 8 mW/cm². The products were analyzed by an Agilent 7820 GC system having a Varian CP7584 column and a Methanizer-FID combination for detection. The only measurable product formed was CO₂. For the analysis of the effect of water vapor on the photocatalytic reaction, the nitrogen flow was send through a water saturator resulting in a propane/oxygen feed of 80% humidity, equivalent to approximately 3.5 vol.% water.

The photocatalytic activity between the samples was compared based on the surface area illuminated. This area was calculated by taking the width and height of the coating. To better validate the obtained photocatalytic activity, the activity of the coatings was calculated by dividing the number of moles of CO₂ produced per hour, by the mass of TiO₂ in the sample. The mass of TiO₂ was derived from the volume of the coating and a TiO₂ density of 2.5 g/cm³ [29]. The volume of the coating was calculated by taking the geometrical surface area and the height of the samples, 400 nm, based on the applied deposition rate of the SCBD.

3. Results

3.1 Morphology and crystallinity

Results of analyses of coatings by Raman spectroscopy are shown in Figure 1. Anatase induces Raman peaks at 145, 194, 398, 515 and 637 cm⁻¹ [34]. The features observed at 445 and 609 cm⁻¹ suggest that also Rutile is present in several samples [34]. Finally, the Si substrate signal can be identified by the peaks at 300, 520 cm⁻¹ and the broad peak around 900–

1000 cm⁻¹. The latter was assigned in the literature to Si–O–Ti bonds [34], but in our study is most likely due to the native oxide of the Si substrate.

Figure 1: Raman spectra of (Left) post annealed and (Right) in-situ annealed TiO₂ films (400nm) in air, annealed at 500, 650 and 800 °C. The spectra are shifted vertically for clarity.

Based on the Raman spectra, the crystal phase of the samples calcined at 500 and 650 °C is Anatase, both for the in situ, as well as the post-annealed samples. No Rutile peaks are present in the spectra of these samples. The post-annealed sample at 800 °C is nearly amorphous, since no Anatase is visible and only very minor Rutile peaks. The in situ calcined sample at 800 °C on the other hand shows very clear Rutile peaks and a minor Anatase peak. Calcination at 800 °C apparently results in a Rutile dominant coating, with minor quantities of Anatase.

The effect of the annealing treatments (in situ and post) on the morphology of the synthesized TiO₂ films is shown in Figures 2 and 3. The average particle size increases for the post annealed sample (Figure 2, panels a–c) from 10 to 40 nm at 500 °C to around 25–100 nm at 650 °C, and 35–180 nm at 800 °C. For the in situ annealed samples particle sizes vary in the ranges of 10–30 nm, 15–130, and 60–200 nm, respectively (Figure 3, panels a–c). The coating structure of the post annealed samples is more open and consists of smaller particles than the dense layers synthesized via in situ annealing. Both in situ and post annealing treatments result in larger particles when higher annealing temperatures are applied.

Figure 2: HR-SEM images of the synthesized TiO_2 films, post annealed in air at **(a)** 500 °C, **(b)** 650 °C and **(c)** 800 °C via direct heating. All the images are displayed at the same scale.

Figure 3: HR-SEM images of the synthesized TiO_2 films, annealed in 10^{-2} mbar O_2 during deposition at **(a)** 500 °C, **(b)** 650 °C and **(c)** 800 °C via direct heating. All the images are displayed at the same scale.

Some differences between the two heating procedures can be observed. The in situ annealed samples (Figure 3) were tightly packed and the particles more rectangular shaped, whereas the post annealed samples (Figure 2) show a more open structure and somewhat more rounded particles.

3.2 Photocatalytic activity

The effect of the annealing temperature on the reaction rate (compared on the basis of the light exposed external surface area of the coating) in propane oxidation is shown in Figure 4. A clear trend can be observed in the reaction rate values, which decreases as a function of increasing annealing temperature, in particular for the samples annealed in the Joules oven. Comparing in situ or post wafer heating at 500 °C and 650 °C, the procedure seems to have very little effect, in agreement with the similar particle size ranges observed at the respective temperatures (Figure 2 and 3). The significantly higher rate of the sample annealed at 500 °C in the oven, rather than by electrical heating will be discussed later. Due to weak

attachment of the TiO₂ coating after post wafer heating at 800 °C, it was not possible to characterize the photocatalytic activity of this sample. The significantly lower rate for the in situ annealed film at 800 °C (as compared to 500 °C and 650 °C) is most likely due to extensive conversion of Anatase into Rutile [35], as observed in the Raman spectra.

Figure 4: Surface area corrected photocatalytic activity of the TiO₂ coating for propane oxidation in the absence and presence of H₂O in the gas mixture, and versus the annealing temperature applied for 1) in situ annealed, 2) post annealed, and 3) post annealed samples in an oven.

To determine whether a small amount of hydroxyl groups on the TiO₂ surface produced by SCBD is limiting the catalytic rate, in Figure 4 also the propane oxidation activity of the post and in situ annealed samples at 500 °C and 650 °C are compared in the presence of water vapor. The humidity of the reaction mixture should promote hole scavenging, thus generating reactive hydroxyl radicals for oxidation. For both samples synthesized at 500 °C the presence of water vapor indeed results in a comparable improvement of the photocatalytic activity. The same effect is seen for the in situ annealed sample at 650 °C, while water resulted in a somewhat lower activity increase for the 650 °C post annealed sample.

A comparison of the reaction rates of the various samples is presented in Table 1. The activity of the quartz glass supported films is 4 times higher as compared to those on the Si substrate, at both annealing temperatures. The difference for the 500 °C wafer-heated sample and the 500 °C quartz sample is even a factor of 6. For the coatings prepared from commercial

TiO₂ powder (Hombikat, 1 mg) on quartz, an even higher activity between 3.5 and 4 mmol/g_{catalyst}/h is obtained (not shown in Table 1).

Table 1: Reaction rates (mmol/hr/g Catalyst) for gas phase photocatalytic propane oxidation

Annealing Temperature	Si-Wafer In-situ annealed (mmol/hr/g)	Si-wafer Post annealed (mmol/hr/g)	Si-wafer post annealed (oven) (mmol/hr/g)	Quartz glass post annealed (oven) (mmol/hr/g)
500 °C	0.15	0.16	0.22	0,93
650 °C	0.15	0.15	0.13	0.62

4. Discussion

Generally, the annealing method (in situ or post electrical heating of the wafer, or post treatment in an oven) has little effect on the morphology obtained and the observed catalytic activity, while activity decreases as a function of increasing annealing temperature. Clearly the used substrate has a much larger effect on the photocatalytic behavior of TiO₂ layers. We speculate that the Si substrate might be an electron acceptor, eventually promoting electron hole recombination at the TiO₂/Si interface and thus reducing photocatalytic efficacy. Based on the band positions of TiO₂ and Si in Figure 5, electrons generated in TiO₂ might be trapped in Si. Since there is no direct interaction with the gas phase, recombination of the trapped electrons is the only alternative. The improved behavior of the samples thermally treated in a Joules oven instead of by wafer-heating at 500 °C, might be related to the formation of a weaker interaction between Si and photocatalyst, perhaps due to a somewhat lower intrinsic temperature, thus leading to a smaller effect of the Si support.

Figure 5: Band positions of TiO₂ (3.2 eV) and Si (1.1. eV)

In addition to the support interaction, remaining differences between samples are most likely related to surface area. Although a specific number cannot be provided for the SCBD samples, the surface area of the Hombikat samples is relatively large [9], providing a relatively high number of OH-groups. It is generally accepted that the amount of OH-groups plays a major role in the activity of TiO₂ materials in gas phase oxidation reactions. The coating of Hombikat powder (on quartz) therefore shows much higher activity than samples prepared by SCBD, despite the fact that the SCBD coatings are well defined, and the films porous. Since the SCBD samples are only exposed to O₂ during synthesis and the reaction mixture does not contain water (vapor), the TiO₂ surface most likely did not have the opportunity to hydrolyze. The results shown in Figure 4, confirm that the presence of water vapor improves the reaction rate, and demonstrates the importance of surface hydroxyl groups. The increase of the reaction rate by a factor of 1.5 is however not sufficient to completely explain the differences between the commercial powders and the synthesized powders, the remaining difference likely due to differences in surface areas.

While the SCBD method has been demonstrated to be flexible and leading to a range of sample morphologies, the application of this method to synthesize layers for subsequent spectroscopic analysis should be considered with caution: we believe this is the first time a strong influence of the substrate (Silicon) has been demonstrated in determining photocatalytic rates, and spectroscopic data might not represent actual

activity of comparable layers on quartz or ceramic substrates, often applied in practical conditions.

5. Conclusions

SCBD coatings supported on Si and thermally treated in the 500 to 650 °C range consist of the Anatase crystal phase with porous morphology. A predominantly Rutile-phase coating, with minor quantities of Anatase, is obtained after calcination at 800 °C.

The SCBD Anatase coatings produced at 500 or 650 °C on Si substrate yield a photocatalytic propane oxidation activity of 0.15 mmol/g_{catalyst}/h, which is significantly lower than obtained for comparable layers on quartz glass (0.6–0.9 mmol/g_{catalyst}/h), suggesting detrimental electron–hole recombination phenomena are occurring at the TiO₂/Si interface. In addition an increase in particle dimensions results in a decrease in photocatalytic activity of the TiO₂ layers. Rutile-phase formation results in additional reduction of photocatalytic activity.

Comparing Hombikat and SCBD produced TiO₂, the latter presumably contains a low density of surface hydroxyl groups, confirmed by the positive effect of water vapor on photocatalytic activity by a factor of 1.5.

References

- [1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, *Nature*, 452 (2008) 301-310.
- [2] D. Zhang, G. Li, J.C. Yu, Inorganic materials for photocatalytic water disinfection, *J. Mater. Chem.*, 20 (2010) 4529-4536.
- [3] P. Usubharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, Photocatalytic Process for CO₂ Emission Reduction from Industrial Flue Gas Streams, *Ind. Eng. Chem. Res.*, 45 (2006) 2558-2568.

- [4] K. Nakata, A. Fujishima, TiO₂ photocatalysis: Design and applications, *J. Photochem. Photobiol., C*, 13 (2012) 169-189.
- [5] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: A review, *Water Res.*, 44 (2010) 2997-3027.
- [6] Z. Xiong, J. Ma, W.J. Ng, T.D. Waite, X.S. Zhao, Silver-modified mesoporous TiO₂ photocatalyst for water purification, *Water Res.*, 45 (2011) 2095-2103.
- [7] N.R. Neti, G.R. Parmar, S. Bakardjieva, J. Subrt, Thick film titania on glass supports for vapour phase photocatalytic degradation of toluene, acetone, and ethanol, *Chem. Eng. J.*, 163 (2010) 219-229.
- [8] J. Peral, X. Domènech, D.F. Ollis, Heterogeneous Photocatalysis for Purification, Decontamination and Deodorization of Air, *J. Chem. Technol. Biotechnol.*, 70 (1997) 117-140.
- [9] J.T. Carneiro, A.R. Almeida, J.A. Moulijn, G. Mul, Cyclohexane selective photocatalytic oxidation by anatase TiO₂: influence of particle size and crystallinity, *Phys. Chem. Chem. Phys.*, 12 (2010) 2744-2750.
- [10] J.J. Murcia, M.C. Hidalgo, J.A. Navío, V. Vaiano, P. Ciambelli, D. Sannino, Ethanol partial photooxidation on Pt/TiO₂ catalysts as green route for acetaldehyde synthesis, *Catal. Today*, 196 (2012) 101-109.
- [11] R.M. Navarro Yerga, M.C. Álvarez Galván, F. del Valle, J.A. Villoria de la Mano, J.L.G. Fierro, Water Splitting on Semiconductor Catalysts under Visible-Light Irradiation, *ChemSusChem*, 2 (2009) 471-485.
- [12] C.-C. Yang, J. Vernimmen, V. Meynen, P. Cool, G. Mul, Mechanistic study of hydrocarbon formation in photocatalytic CO₂ reduction over Ti-SBA-15, *J. Catal.*, 284 (2011) 1-8.
- [13] O.K. Varghese, M. Paulose, T.J. LaTempa, C.A. Grimes, High-Rate Solar Photocatalytic Conversion of CO₂ and Water Vapor to Hydrocarbon Fuels, *Nano Lett.*, 9 (2009) 731-737.
- [14] A. Sclafani, J.-M. Herrmann, Influence of metallic silver and of platinum-silver bimetallic deposits on the photocatalytic activity of titania (anatase and rutile) in organic and aqueous media, *J. Photochem. Photobiol., A*, 113 (1998) 181-188.

- [15] B. Ohtani, Preparing Articles on Photocatalysis—Beyond the Illusions, Misconceptions, and Speculation, *Chem. Lett.*, 37 (2008) 216-229.
- [16] A. Kubacka, M. Fernández-García, G. Colón, Advanced Nanoarchitectures for Solar Photocatalytic Applications, *Chem. Rev.*, 112 (2011) 1555-1614.
- [17] E. Barborini, A.M. Conti, I. Kholmanov, P. Piseri, A. Podestà, P. Milani, C. Cepek, O. Sakho, R. Macovez, M. Sancrotti, Nanostructured TiO₂ Films with 2 eV Optical Gap, *Adv. Mater.*, 17 (2005) 1842-1846.
- [18] M.V. Dozzi, E. Selli, Doping TiO₂ with p-block elements: Effects on photocatalytic activity, *J. Photochem. Photobiol., C*, 14 (2013) 13-28.
- [19] M. Chiodi, C.P. Cheney, P. Vilmercati, E. Cavaliere, N. Mannella, H.H. Weitering, L. Gavioli, Enhanced Dopant Solubility and Visible-Light Absorption in Cr–N Codoped TiO₂ Nanoclusters, *J. Phys. Chem. C*, 116 (2011) 311-318.
- [20] A. Naldoni, M. D'Arienzo, M. Altomare, M. Marelli, R. Scotti, F. Morazzoni, E. Selli, V. Dal Santo, Pt and Au/TiO₂ photocatalysts for methanol reforming: Role of metal nanoparticles in tuning charge trapping properties and photoefficiency, *Appl. Catal., B*, 130–131 (2013) 239-248.
- [21] J.T. Carneiro, T.J. Savenije, G. Mul, Experimental evidence for electron localization on Au upon photo-activation of Au/anatase catalysts, *Phys. Chem. Chem. Phys.*, 11 (2009) 2708-2714.
- [22] M.A. Henderson, A surface science perspective on photocatalysis, *Surf. Sci. Rep.*, 66 (2011) 185-297.
- [23] A.N. Mangham, N. Govind, M.E. Bowden, V. Shutthanandan, A.G. Joly, M.A. Henderson, S.A. Chambers, Photochemical Properties, Composition, and Structure in Molecular Beam Epitaxy Grown Fe “Doped” and (Fe,N) Codoped Rutile TiO₂(110), *J. Phys. Chem. C*, 115 (2011) 15416-15424.
- [24] W.-J. Yin, H. Tang, S.-H. Wei, M.M. Al-Jassim, J. Turner, Y. Yan, Band structure engineering of semiconductors for enhanced photoelectrochemical water splitting: The case of TiO₂, *Phys. Rev. B*, 82 (2010) 045106.

- [25] E. Barborini, P. Piseri, P. Milani, Pulsed microplasma source of high intensity supersonic carbon cluster beams, *J. Phys. D: Appl. Phys.*, 32 (1999) L105-L109.
- [26] E. Karabudak, R. Kas, W. Ogieglo, D. Rafieian, S. Schlautmann, R.G.H. Lammertink, H.J.G.E. Gardeniers, G. Mul, Disposable Attenuated Total Reflection-Infrared Crystals from Silicon Wafer: A Versatile Approach to Surface Infrared Spectroscopy, *Anal. Chem.*, 85 (2012) 33-38.
- [27] A.R. Almeida, J.A. Moulijn, G. Mul, In Situ ATR-FTIR Study on the Selective Photo-oxidation of Cyclohexane over Anatase TiO₂, *J. Phys. Chem. C*, 112 (2008) 1552-1561.
- [28] B. Hauchecorne, S. Lenaerts, Unravelling the mysteries of gas phase photocatalytic reaction pathways by studying the catalyst surface: A literature review of different Fourier transform infrared spectroscopic reaction cells used in the field, *J. Photochem. Photobiol., C*, 14 (2013) 72-85.
- [29] F. Della Foglia, T. Losco, P. Piseri, P. Milani, E. Selli, Photocatalytic activity of nanostructured TiO₂ films produced by supersonic cluster beam deposition, *J. Nanopart. Res.*, 11 (2009) 1339-1348.
- [30] T. Mazza, E. Barborini, I.N. Kholmanov, P. Piseri, G. Bongiorno, S. Vinati, P. Milani, C. Ducati, D. Cattaneo, A.L. Bassi, C.E. Bottani, A.M. Taurino, P. Siciliano, Libraries of cluster-assembled titania films for chemical sensing, *Appl. Phys. Lett.*, 87 (2005) 103108-103103.
- [31] E. Barborini, I.N. Kholmanov, P. Piseri, C. Ducati, C.E. Bottani, P. Milani, Engineering the nanocrystalline structure of TiO₂ films by aerodynamically filtered cluster deposition, *Appl. Phys. Lett.*, 81 (2002) 3052-3054.
- [32] M. Chiodi, E. Cavaliere, I. Kholmanov, M. Simone, O. Sakho, C. Cepek, L. Gavioli, Nanostructured TiO_x film on Si substrate: room temperature formation of TiSi_x nanoclusters, *J. Nanopart. Res.*, 12 (2010) 2645-2653.
- [33] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, Toward a Physically Sound Structure–Activity Relationship of TiO₂-Based Photocatalysts, *J. Phys. Chem. C*, 114 (2009) 327-332.

- [34] V.V. Yakovlev, G. Scarel, C.R. Aita, S. Mochizuki, Short-range order in ultrathin film titanium dioxide studied by Raman spectroscopy, *Appl. Phys. Lett.*, 76 (2000) 1107-1109.
- [35] C.G. Silva, J.L. Faria, Anatase vs. rutile efficiency on the photocatalytic degradation of clofibric acid under near UV to visible irradiation, *Photochem. Photobiol. Sci.*, 8 (2009) 705-711.

4

THE CATALYST DEPENDENT EFFECT OF OXYGEN PARTIAL PRESSURE ON RATES IN GAS PHASE PHOTOCATALYTIC OXIDATION OF PROPANE

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Fraters, B.D., Beijeman, M., Mul, G., The catalyst dependent effect of oxygen partial pressure on rates in gas phase photocatalytic oxidation of propane

Abstract:

TiO₂ of variable surface area and crystallinity was prepared by calcination at elevated temperatures in the range of 200 to 600 °C. The oxygen dependency of photocatalytic activity in propane oxidation of these samples was found to be strongly depending on the calcination temperature. For the photocatalytic gas phase oxidation of propane over non-annealed Hombikat (H0), an optimum in activity was found at 2 vol.% oxygen, whereas for the catalyst annealed at 600 °C (H600) the highest activity was obtained for oxygen concentrations above 10 vol.%. The photonic efficiencies at low (2 vol.%) and high (20 vol.%) oxygen concentrations were determined at respectively 2.1% and 1.3% for H0, and at 1.2% and 1.9% for H600. We discuss these different photonic efficiency dependencies on oxygen concentration on the basis of the physico-chemical properties of the photocatalysts, in particular surface OH-groups and crystallinity. On the one hand, a high O₂ concentration is favorable for highly (crystalline) structures of TiO₂, to assure quick consumption of electrons, and to decrease probability of internal charge recombination. On the other hand, for samples with a high OH⁻ surface group density (and relatively low crystallinity), a high O₂ (surface) concentration (>10 vol.%) favors external charge recombination, induced by a relatively low surface propane concentration, and governed by the reaction of superoxide anions with hydroxyl radicals, yielding oxygen and hydroxyl anions.

1. Introduction

Based on the number of patents, air purification is the application of photocatalysis closest to commercialization [1]. However, when the research in the field of photocatalytic gas phase treatment is considered, still a number of important challenges need to be solved. The main problems associated with TiO_2 , the most generally used photocatalyst, are i) the large band gap and ii) the high rate of electron-hole recombination [2]. Electron-hole recombination rates depend on crystallinity of the catalyst [3, 4], and on the coverage of the surface with OH-groups [5, 6]. A positive effect of a higher crystallinity of the photocatalyst, is generally ascribed to a low concentration of defects within the photocatalyst crystals, inducing a low probability of electron hole recombination[7]. At the same time, the presence of OH-groups on the surface is seen as essential for photocatalytic reactions [8, 9]. First of all, these groups are able to react with holes, creating OH radicals, which are very effective in hydrocarbon oxidation [5], thus improving the photonic efficiency [10]. Secondly, the presence of OH-groups improves catalyst stability, presumably by destabilizing carbonate species formed on the surface of the semiconductor (TiO_2) upon light induced reaction of oxygen/hydrocarbon mixtures [6]. To obtain highly crystalline materials, often annealing is required. Unfortunately, annealing results in a decreasing quantity of OH-groups, associated with a decreasing surface area and increasing particle size of TiO_2 [4, 11]. Therefore, the annealing temperature for optimized performance of the catalyst is typically a trade-off between obtained crystallinity, surface area, and quantity of OH groups. Several research groups have analyzed this trade-off.

Table 1: Summary of characterization data reported by Carneiro [11]. Surface hydroxyl group concentrations were obtained by NH_3 -TPD. In addition surface area, particle diameter, number of hydroxyl groups per particle, product of the charge carrier formation and the sum of electron and hole mobilities, $\eta \sum \mu_i$ and halftime, $\tau_{1/2}$, of the materials studied at a laser pulse intensity of $15.6 \mu\text{J}/\text{cm}^2$ and 337 nm wavelength, are reported

	S_{BET} (m^2/g)	[OH] ($\text{mmol}/\text{g}_{\text{cat}}$)	d_p (nm)	OH_{pp} ($10^3/\text{particle}$)	$\eta \sum \mu_i^*$ ($10^{-3}/\text{cm}^2/\text{V/s}$)	$\tau_{1/2}$ (μs)
H	337	1.15	7	0.32	0.7	0.1
H200	306	0.92	9	0.49	-	-
H400	167	0.69	13	1.26	0.7	0.3
H600	73	0.34	19	3.05	13.8	> 4.7

* Values for pulse intensity, I_0 , of 4×10^{12} Photons/ cm^2 /pulse¹

In the work of Carneiro [11], the relation between OH-groups and crystallinity was investigated for Hombikat catalysts, and an annealing temperature of 600 °C was found for optimized activity in the liquid phase oxidation of methylene blue. In the work of van der Meulen et al. [12], the photocatalytic oxidation of propane in the gas phase was analyzed by FTIR spectroscopy for TiO_2 photocatalysts with different crystallinities (and surface properties). Depending on the composition of the catalyst, either more formate (rutile), or acetone (anatase) was observed. The highest activity was observed for a mixture of rutile and large anatase particles, and the lowest activity for small anatase particles. The latter was assigned to a relatively high surface coverage of intermediates, inhibiting reaction. Furthermore, Di Paola et al. [13] compared TiO_2 photocatalysts with different crystallinities and OH-group concentrations in the photodegradation of 4-nitrophenol and the selective oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde under UV irradiation. A higher rate of 4-NP degradation was exhibited by the most crystalline commercial samples, whereas the highest selectivity toward the synthesis of p-anisaldehyde was obtained by the powders exhibiting the least crystallinity, and the highest concentrations of OH-groups.

The importance of a high crystallinity and the presence of OH-groups is typically discussed in relation to the faith of holes, but also the efficiency of transfer of electrons needs to be addressed [14]. An electron acceptor is required [13], which is typically oxygen in the case of gas phase oxidation processes [15]. The influence of oxygen concentration on the overall rate of gas phase reactions, in relation to the physico-chemical properties of the photo-catalysts, has to the best of our knowledge received little attention. Therefore, in this chapter we address the effect of oxygen concentration on photocatalytic performance of TiO_2 , in relation to the OH-group concentration and crystallinity, in more detail. We will demonstrate that the optimum oxygen concentration for reactivity depends on the temperature at which TiO_2 has been annealed, and discuss some tentative explanations for this phenomenon.

2. Experimental set-up

2.1 Catalyst preparation.

As starting material, commercial Hombikat UV100 (Sachtleden), 100% anatase was used. The TiO_2 powder was annealed according to the method described in the work of Carneiro [11], at 200, 400 and 600 °C for 2 hours (heating rate 10 K min⁻¹) in a Joules oven (Carbolite CWF 1100). The most important characteristics of the TiO_2 photocatalysts Hombikat annealed at different temperatures were analyzed by Carneiro [11], and shown in Table 1. For the synthesis of the coatings used for catalyst evaluation, the resulting powders were suspended in 25 ml of distilled water with a concentration of 2 g/l. After treatment in an ultrasonic bath for 30 minutes (VWR Ultrasonic cleaner), the emulsion was drop-casted on a glass substrate. The coatings were dried under vacuum in a desiccator containing silica gel overnight at ambient temperatures, resulting in a coating containing approximately 2 mg of catalyst. This value was calculated based on volume and concentration of the TiO_2 suspension, and confirmed to vary by a maximum amount of 5% by scraping of, and measuring the weight of the deposited catalysts on a micro balance (Mettler AE 163).

2.2 Photocatalytic reactor system.

The analysis of the photocatalytic activity of the coatings was performed in a 2 ml top illuminated batch reactor, closed with a quartz window. The reactor was illuminated by a 365 nm LED (Roithner LaserTechnik, Austria) with a maximum light intensity of 25 mW/cm² at the catalyst surface. A photospectrometer (HR4000, OceanOptics) was used to probe the light intensity at the position where the sample would be located, and the intensity calibrated to the current sent through the LED. The reactor was fed with a 30 ml/min flow of a predefined gas mixture of propane and O₂, prepared by a combination of mass flow controllers. After a fixed interval of 5 minutes reaction time, the complete gas mixture was purged into an Agilent 7820 GC system, having a Varian CP7584 column and a Methanizer-FID combination for detection.

The O₂ concentration was varied between 0-19.5% and the propane concentration between 0.5-2%. Furthermore the light intensity was varied between 0-25 mW/cm². The reaction rates were calculated both for the variation of the light intensity, and the oxygen concentration. For the calculations of the reaction rates, the CO₂ concentration determined after a reaction time of 5 minutes was used, since this is representative of the initial reaction rate, while also sufficient concentration was obtained to calculate rates accurately.

$$r = \frac{P_{tot} \cdot X_{CO_2} \cdot V}{R \cdot T} \cdot \frac{1}{m} \cdot \frac{60}{t} \quad (1)$$

$$X_{CO_2} = \frac{CO_2}{10^6} \quad (2)$$

The reaction rate, r (mmol/g/hr) of the coating was calculated by equation 1, where P_{tot} is the pressure in the reactor (Pa), V is the volume of the reactor (m³), R the gas constant (m³ Pa/mol K), m the catalyst mass (g) and t the reaction time (min). X_{CO_2} is the fraction of CO₂ of the gas mixture, and is calculated by equation 2, where CO_2 is the measured CO₂ concentration in ppm after 5 minutes of illumination. The concentration of CO₂ after 5

minutes of exposure of the propane/oxygen mixture to the coating in the dark, was also measured and no activity was observed.

The photonic efficiencies of the reaction were calculated via the oxygen consumption rates, required to convert propane to CO_2 and H_2O . Since oxygen is only consumed in this reaction, based on the CO_2 production the oxygen consumption was calculated. Each oxygen molecule was assumed to require one photo-activated electron to form a super oxide anion (O_2^-) [16], giving the electron consumption. The number of moles of photons (maximum available electrons) was calculated based on the light intensity on the surface of the photocatalyst and the wavelength. The photonic efficiency was obtained by dividing the oxygen consumption (electrons used in reaction) by the number of photons introduced in the system after specific time of reaction.

3. Results

3.1 *Effect of Oxygen concentration*

The activity of the different photocatalysts as a function of oxygen concentration at fixed maximum light intensity (25 mW/cm^2), is shown in Figure 1. Clearly, sample dependent oxygen concentration effects can be observed. For the H0 sample, and to minor extent for the H200 sample, the photocatalytic reaction rate maximizes at respectively 2 vol.% and 5 vol.%, and decreases at higher oxygen concentrations. H600, and to lesser extent H400, show a different trend. In both cases the activity increases relatively slowly as a function of increasing oxygen concentration, up to roughly 10 vol.% oxygen. Further increasing the oxygen concentration does not seem to affect the photocatalytic activity significantly.

Figure 1: Reaction rate vs oxygen concentration achieved at 25 mW/cm^2 for a 0.5 vol.% propane concentration on TiO_2 and TiO_2 annealed at, 200, 400 and 600 °C

Based on the data presented in Figure 1, at 2 vol.% oxygen, H0 and H600 reach efficiencies of respectively 2.1% and 1.3%, and at 20 vol.% oxygen respectively 1.2% and 1.9%.

3.2 Effect of light intensity

In Figure 2 (Left), the effect of light intensity on the reaction rate is shown for an oxygen concentration of 19.5 vol.%. For all light intensities, H600 has the highest activity and H0 the lowest. For H200 and H400 intermediate rates were determined, of which the difference is small. The slope of the curves represents the photonic efficiency, which appears not to be constant and to slightly decrease at increased light intensities. In other words, the order of the reaction rate with respect to light intensity is somewhat smaller than 1 at the higher intensities. When focusing in more detail on the H0 and H600 catalysts, some interesting differences in the reaction rate can be observed at 1% oxygen, as shown in Figure 2 (Right).

Figure 2: CO₂ production rate (r) as a function of light intensity for the photocatalytic oxidation of propane (**Left**) at 20% oxygen on TiO₂, and TiO₂ annealed at 200, 400 and 600 °C, respectively and (**Right**) at 1% oxygen on TiO₂ and TiO₂ annealed at 600 °C.

Whereas for H600 the activity increases gradually as a function of increasing light intensity, for H0 initially a steep increase in activity is observed (first order light intensity behavior) and constant photonic efficiency) until an intensity of about 10 mW/cm² is reached, after which the activity increases no further (zero order light intensity behavior). However, up to 25 mW/cm² H0 remains the more active catalyst, as expected on the basis of Figure 1.

3.3 Effect of propane concentration

The effect of the propane concentration on the reaction rate was studied for H600 and H0. In Figure 3, the reaction rates for different propane concentrations as function of light intensity are shown. The oxygen concentration was 20%, and it can be clearly observed that increasing the propane concentration results in a higher activity for both catalyst compositions. For an oxygen concentration of 1%, increasing the propane concentration did not result in significantly higher activity, neither for H600, nor for H0 (not shown).

Figure 3: CO₂ production rate (r) versus light intensity for the photocatalytic oxidation of 0.5, 1 and 2% propane at 20% oxygen (**Left**) on TiO₂ annealed at 600 °C and (**Right**) on TiO₂ H(0).

4. Discussion

The important effects of OH-groups, adsorbed quantity of oxygen, and crystallinity of the photocatalysts on the activity are revealed by the variation of the oxygen concentration and light intensity as shown in Figures 1 and 2. Whereas for H0 the highest activity is observed around 2% oxygen, and the activity decreases for higher O₂ concentrations, for H600, above 10% oxygen the activity is highest and relatively similar.

Figure 4: CO₂ production rate (r) versus annealing temperature of TiO₂ for the photocatalytic oxidation of 0.5% propane at 2 and 20% oxygen (at 25 mW intensity).

In Figure 4, the activity of the photocatalyst is plotted as function of the calcination temperature for the two most interesting oxygen concentrations from Figure 1. Two completely different trends can be observed in this manner. In the case of 20% oxygen, the activity increases almost linearly as a function of increasing annealing temperature. However, in the case of 2% oxygen the activity decreases from H0-H400, but suddenly increases for H600. The text depicted in Figure 4 is further elaborated on in the following. First, the trend in 2% oxygen is discussed.

The decreasing rate observed for catalysts annealed at elevated temperatures in the range of 0 to 400 °C can be explained on the basis of the following. Besides the extent of electron hole separation within the bulk of the catalyst, two other important factors play a role in determining photocatalytic activity. First of all, the concentration of surface hydroxylgroups of the photocatalyst, and secondly the electron scavenging efficiency of the electrons by oxygen. These effects can be summarized in the following reactions [2, 5, 13], (s) indicating surface adsorbed species:

One of the major differences between H0 and H600 is the particle size (7 vs. 19 nm [11], Table 1), meaning that the surface area of H0 is significantly larger than of H600, and with that the OH-surface concentration favoring reaction (2). Due to this higher surface area, H0 is also able to adsorb a relatively high quantity of oxygen, improving the transfer of electrons to oxygen according to reaction (1). The negative trend in rate for increasing annealing temperatures till 400 °C, shown in figure 4, can be explained on the basis of the work of Carneiro [11], indicating that by annealing, the concentration of OH-groups reduces significantly (Table 1). The presence of OH-groups is seen as essential for the photocatalytic oxidation, and the activity decrease in agreement with this trend. Obviously the quantity of adsorbed oxygen will also decrease with a decreasing surface area of these samples, contributing to the decreasing activity trend. The sudden activity increase in activity for H600, is a result of the significantly improved electron hole separation capacity, again in agreement with data reported by Carneiro et al [11], who showed by time resolved microwave conductivity data that the concentration of mobile electrons is significantly larger in TiO₂ of high crystallinity (Table 1).

The deviations from these phenomena at 20% oxygen are somewhat more difficult to explain. As already mentioned H0 has a large OH-group population, whereas also the oxygen surface concentration for H0 will be high at 20 vol.% oxygen, likely limiting the concentration of adsorbed propane. The latter assumption is in agreement with the observation that a higher propane partial pressure leads to a higher rate of reaction (Figure 5). We already reasoned that for H0 a significant amount of OH-radicals will be present, formed by reaction (2). We now assume that at 20% the concentration of $O_2^{\bullet-}$ will be that high, that a detrimental reaction will occur, illustrated by equation 4. What actually happens is 'external

recombination' of the electron and hole [17], or in other words, a radical termination reaction :

The increasing trend in activity with annealing temperature is then explained by a decreasing OH concentration, decreasing the probability of equation (4) to occur, and favoring hole transfer to adsorbed propane according to reaction (3). Furthermore, as is illustrated in Figure 5, the lower concentration and density of OH-groups on H600 means that the distance between the OH and oxygen radicals increases, further reducing the chance of external (surface) recombination. Finally, the favorable crystalline properties of H600 assist in the high activity, observed by the slight deviation from linearity comparing H400 and H600.

Figure 5: Schematic representation **(Left)** of a H600 particle and **(Right)** of an H0 particle, and the effect of particle size in combination with OH concentration on external recombination of O₂ and OH-radicals. Images are based on the data presented in Table 1.

5. Conclusions

The oxygen dependency of photocatalytic activity in propane oxidation of TiO_2 was found to be strongly depending on the morphology. The H0 catalyst, of low crystallinity and containing a high OH-group concentration, showed an optimum in activity at an oxygen concentration of 2 vol.%, whereas for H600 a high activity was obtained for oxygen concentrations above 10 vol.%. The photonic efficiencies at low (2 vol.%) and high (20 vol.%) oxygen concentrations were determined at respectively 2.1% and 1.3% for H0, and at 1.2% and 1.9% for H600. Differences in surface OH-group density and crystallinity of the various TiO_2 samples are at the origin of this different behavior. On the one hand, a high O_2 concentration is favorable for highly (crystalline) structures of TiO_2 , to assure quick consumption of electrons, and to decrease probability of internal charge recombination. On the other hand, for samples with a high OH^- surface group density, a high O_2 (surface) concentration (>10 vol.%) favors external charge recombination, the result of reaction of superoxide anions with hydroxyl radicals, yielding oxygen and hydroxyl anions. Reduction of the OH group density leads to less recombination, and likely favors the transfer of holes directly to adsorbed propane molecules.

References

- [1] Y. Paz, Application of TiO_2 photocatalysis for air treatment: Patents' overview, *Appl. Catal., B*, 99 (2010) 448-460.
- [2] M.A. Henderson, A surface science perspective on photocatalysis, *Surf. Sci. Rep.*, 66 (2011) 185-297.
- [3] M. Ouzzine, M.A. Lillo-Ródenas, A. Linares-Solano, Photocatalytic oxidation of propene in gas phase at low concentration by optimized TiO_2 nanoparticles, *Appl. Catal., B*, 134–135 (2013) 333-343.

- [4] Z. Pap, É. Karácsanyi, Z. Cegléd, A. Dombi, V. Danciu, I.C. Popescu, L. Baia, A. Oszkó, K. Mogyorósi, Dynamic changes on the surface during the calcination of rapid heat treated TiO₂ photocatalysts, *Appl. Catal., B*, 111–112 (2012) 595-604.
- [5] K. Chhor, J.F. Bocquet, C. Colbeau-Justin, Comparative studies of phenol and salicylic acid photocatalytic degradation: influence of adsorbed oxygen, *Mater. Chem. Phys.*, 86 (2004) 123-131.
- [6] C. Häggglund, B. Kasemo, L. Österlund, In Situ Reactivity and FTIR Study of the Wet and Dry Photooxidation of Propane on Anatase TiO₂, *J. Phys. Chem. B*, 109 (2005) 10886-10895.
- [7] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, How Phase Composition Influences Optoelectronic and Photocatalytic Properties of TiO₂, *J. Phys. Chem. C*, 115 (2011) 2211-2217.
- [8] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, Photocatalytic oxidation of gaseous toluene on anatase TiO₂ catalyst: mechanistic aspects and FT-IR investigation, *Appl. Catal., B*, 20 (1999) 15-27.
- [9] J. Araña, A.P. Alonso, J.M.D. Rodríguez, G. Colón, J.A. Navío, J.P. Peña, FTIR study of photocatalytic degradation of 2-propanol in gas phase with different TiO₂ catalysts, *Appl. Catal., B*, 89 (2009) 204-213.
- [10] A.K. Boulamanti, C.J. Philippopoulos, Photocatalytic degradation of methyl tert-butyl ether in the gas-phase: A kinetic study, *J. Hazard. Mater.*, 160 (2008) 83-87.
- [11] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, Toward a Physically Sound Structure–Activity Relationship of TiO₂-Based Photocatalysts, *J. Phys. Chem. C*, 114 (2009) 327-332.
- [12] T. van der Meulen, A. Mattson, L. Österlund, A comparative study of the photocatalytic oxidation of propane on anatase, rutile, and mixed-phase anatase–rutile TiO₂ nanoparticles: Role of surface intermediates, *J. Catal.*, 251 (2007) 131-144.
- [13] A. Di Paola, M. Bellardita, L. Palmisano, Z. Barbieriková, V. Brezová, Influence of crystallinity and OH surface density on the photocatalytic activity of TiO₂ powders, *J. Photochem. Photobiol., A*, 273 (2014) 59-67.

- [14] Y. Nosaka, M. Kishimoto, J. Nishino, Factors Governing the Initial Process of TiO₂ Photocatalysis Studied by Means of in-Situ Electron Spin Resonance Measurements, *J. Phys. Chem. B*, 102 (1998) 10279-10283.
- [15] B. Hauchecorne, S. Lenaerts, Unravelling the mysteries of gas phase photocatalytic reaction pathways by studying the catalyst surface: A literature review of different Fourier transform infrared spectroscopic reaction cells used in the field, *J. Photochem. Photobiol., C*, 14 (2013) 72-85.
- [16] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, Photocatalytic purification of volatile organic compounds in indoor air: A literature review, *Atmos. Environ.*, 43 (2009) 2229-2246.
- [17] G. Munuera, V. Rives-Arnau, A. Saucedo, Photo-adsorption and photo-desorption of oxygen on highly hydroxylated TiO₂ surfaces. Part 1.-Role of hydroxyl groups in photo-adsorption, *J. Chem. Soc., Faraday Trans. 1*, 75 (1979) 736-747.

5

HOW PT NANOPARTICLES AFFECT TiO₂-INDUCED GAS PHASE PHOTOCATALYTIC OXIDATION REACTIONS

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Abstract

The effect of Pt nanoparticles on the gas phase photocatalytic oxidation activity of TiO_2 is shown to be largely dependent on the molecular functionality of the substrate. We demonstrate that Pt nanoparticles decrease rates in photocatalytic oxidation of propane, whereas a strong beneficial effect of Pt was observed in oxidation of ethanol. On the basis of oxygen conversion, Pt nanoparticles result in an increase in rates of TiO_2 from 1.55 mmol $\text{O}_2/\text{g/hr}$ to 4.65 mmol $\text{O}_2/\text{g/hr}$, at a light intensity of 8 mW/cm^2 at 375 nm. The latter value is comparable to obtained in propane oxidation in the absence of Pt, and represents a photonic efficiency of approximately 2 %. Besides an effect on oxygen conversion rate, we also observed significant effects of Pt nanoparticles on reaction selectivity. DRIFT analysis demonstrates that acetone is a rather abundant surface bound intermediate when propane is oxidized in the presence of Pt nanoparticles, while this is barely observed in the absence of Pt nanoparticles. In ethanol oxidation, both surface bound and gas phase acetaldehyde are produced more significantly in the presence than in the absence of Pt. The activity data are discussed on the basis of adsorption affinity of the reactants towards TiO_2 , much higher for ethanol as compared to propane. The changes in (surface) selectivity are discussed on the basis of Pt induced alterations in the rate determining steps.

1. Introduction

Titanium dioxide has been studied extensively in gas phase photocatalytic oxidation of volatile organic compounds (VOC's) [1, 2]. Depending on the process conditions, partial oxidation products can be obtained, such as acetaldehyde by oxidation of ethanol. Alternatively, complete degradation to CO₂ has been observed, typically the case for conversion of aliphatic hydrocarbons. With the aim to improve photocatalytic performance, TiO₂ is often functionalized with metallic nanoparticles. However, in gas phase oxidation of hydrocarbons, positive, as well as negative effects of these nanoparticles have been observed. Addition of Pt nanoparticles (NPs) has been reported to result in an improvement in activity in gas phase oxidation of alcohols, acids and esters, as summarized in a review article by Henderson [3], and e.g. reported by Blount et al. [4], whereas Murcia et al. [5], and Sano et al. [6] observed negative effects of Pt nanoparticles in the TiO₂ catalyzed gas phase oxidation of respectively cyclohexane and acetaldehyde. In the cases in which positive effects of Pt NPs have been observed, usually two phenomena are advocated. The first is based on changes observed in the physical behavior of TiO₂, i.e. Pt extends lifetimes of photo-excited states. These lifetimes have for example been determined by fluorescence measurements or Time Resolved Microwave Conductivity Measurements (TRMC) [7, 8]. The other explanation is to assign promotion purely to catalytic effects: Pt catalyzes reduction of oxygen to super oxide anion radicals, and therefore promotes the overall reaction rate in hydrocarbon oxidation.

It should be mentioned that comparing rates on the basis of hydrocarbon conversion is not trivial: while the apparent rate of the conversion of a hydrocarbon might be higher, alcohols typically form partially oxidized products with high selectivity (e.g. acetone in the case of iso-propanol), whereas alkanes are predominantly converted to CO₂, requiring significantly higher quantities of oxygen *per* hydrocarbon molecule to be activated and converted.

In this chapter we report on the effect of addition of Pt NPs on the photocatalytic activity of TiO_2 for two reactants with different molecular functionality, i.e. ethanol and propane. Furthermore, the effect of reaction conditions, i.e. oxygen concentration, light intensity and the content of water vapor on the conversion rates induced by both TiO_2 and Pt-TiO_2 , will be addressed. We will compare the data specifically on the basis of oxygen conversion, activation of which is an important intermediate step in photocatalytic oxidation. This also allows the photonic efficiency to be evaluated. Further, by means of Diffuse Reflectance Infrared Spectroscopy we have analyzed the presence of surface intermediates in both reactions when catalyzed by TiO_2 or Pt-TiO_2 . The results will be discussed on the basis of competitive adsorption phenomena, suggesting a positive effect of Pt can be mainly assigned to providing oxygen reduction sites in the case of strongly adsorbing reactants on TiO_2 . The catalytic effect of Pt is corroborated by the huge differences observed in (surface) selectivity in the oxidation reactions of propane or ethanol.

2. Experimental set-up

2.1 Catalyst preparation

Commercial Hombikat UV100 (Sachtleben), 100% Anatase TiO_2 , was annealed at 600 °C for 2 hours (heating rate 10 K min⁻¹) in a Joules oven (Carbolite CWF 1100) to obtain a highly active Anatase powder [9]. For the synthesis of well-defined Pt nanoparticles (NP's) the method described in detail by Baranova et al. was used [10]. First a 0.2 M NaOH ethylene glycol solution was prepared and stirred overnight. Then Chloroplatinic(IV)acid-hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) (Sigma-Aldrich), equivalent for the preparation of a 1 wt.% loading of Pt, was dissolved in the ethylene glycol solution and heated to 160 °C in a silicon oil bath for 20 minutes. The solution was subsequently cooled to room temperature in a water bath. TiO_2 (100 mg) was suspended in 50 ml water (mQ). The suspension was treated for 20 minutes in an ultrasonic bath (VWR Ultrasonic cleaner), and added to the cooled precursor solution of Pt nanoparticles. After 5 minutes stirring, a 2

M sulfuric acid solution was added drop wise and the mixture stirred for another 2 hours. The powder was filtered and washed extensively with mQ water. Finally, freeze drying of the catalyst was applied.

For the synthesis of a coating on glass plates, the obtained material was suspended in mQ water and treated in an ultrasonic bath for 30 minutes. The suspension was coated on the glass substrates by drop casting, and water removed under vacuum in a desiccator containing silica gel. Each glass substrate contained ~1 mg of catalyst. This value was calculated based on volume and concentration of the TiO₂ suspension, and confirmed to vary by a maximum amount of 5% by scraping of, and measuring the weight of the deposited catalysts on a micro balance (Mettler AE 163).

2.2 Characterization of the catalysts

The deposition of Pt nanoparticles on the Hombikat catalyst was analyzed by TEM measurements performed on a Philips CM300ST-FEG Transmission Electron Microscope, equipped with a Noran System Six EDX analyzer.

2.3 Photocatalytic reactor system

The prepared photocatalytic coatings were analyzed in a 2 ml top illuminated batch reactor, equipped with a quartz window. As illumination source, a 375 nm LED (Roithner LaserTechnik, Austria, APG2C1-375-S) was used with a maximum possible light intensity at the catalyst surface of 8 mW/cm². A photospectrometer (HR4000, Ocean Optics) was used to probe the light intensity at the position where the sample would be located, and the intensity calibrated to the current sent through the LED. The reactor was operated in batch mode, after 30 ml/min of a predefined mixture was fed, prepared by a combination of mass flow controllers (propane and O₂) and, if applicable, liquid evaporation (ethanol and water). Subsequently two valves were used to close the reactor, and illumination was initiated. After fixed time intervals of illumination, the entire gas composition present in the reactor was purged by He flow onto a Varian CP7584 column coupled to

a Methanizer-FID combination for detection of (oxidized) hydrocarbons, CO, and CO₂, both present in an Agilent 7820 GC system. Oxygen consumption was calculated on the basis of the quantification of these products.

For analysis of propane oxidation, typically a concentration of 0.5 vol.% was used, and for ethanol a concentration of 1.1 vol.%. The O₂ concentration was varied between 0 and 19.5 vol.%, and the humidity of the gas mixture was set at either 0% or 40%. The standard reaction conditions used as reference point were respectively 0.5 vol.% propane, 19.5 vol.% oxygen, 0% water vapor, and a light intensity of 8 mW/cm². Furthermore, the Pt-TiO₂ catalyst was analyzed for the presence of organic residues remaining after synthesis by exposing the catalyst to UV-light and synthetic air in the batch reactor, and measuring the amount of CO₂ formed.

The reaction rates were calculated from the concentrations of the products determined after 5 minutes of exposure to light. This time was chosen to compare catalyst activity in various reaction conditions, because linearity in growth of product concentration was observed in this time interval, and sufficient conversion (~ 30%) occurred to obtain accurate data.

$$r = \frac{P_{tot} \cdot X_{CO_2} \cdot V}{R \cdot T} \cdot \frac{1}{m} \cdot \frac{60}{t} \quad (1)$$

$$X_{CO_2} = \frac{CO_2 - CO_{2(dark)}}{10^6} \quad (2)$$

The reaction rate, r (mmol/g/hr) of the coating was calculated by equation 1, where P_{tot} is the pressure in the reactor (10⁵ Pa), V is the volume of the reactor (2 x 10⁻⁶ m³), R the gas constant (8.314 m³ Pa/mol K), m the catalyst mass (1 x 10⁻³ g), and t the reaction time (5 min). X_{CO_2} is the quantity of produced CO₂ in the gas mixture after 5 minutes, and was calculated by equation 2, where CO₂ and CO_{2(dark)} were measured concentrations in ppm. During the experiments, a reaction at standard conditions was performed between the series, to ensure that no deactivation of the catalyst layer had occurred, and the data obtained were representative of the behavior of a pristine catalyst layer.

2.4 In-situ DRIFT spectroscopy

Photocatalytic ethanol and propane oxidation were analyzed by IR spectroscopy using a Bruker Vertex 70 spectrometer equipped with a Liquid N₂ cooled MCT detector, and a Harrick Praying Mantis diffuse reflectance accessory containing a three window cell. One window (Quartz) allowed the illumination of the catalyst formulation with UV/Vis light, while two ZnSe windows provided an optical path for infrared analysis. Prior to the illumination experiments, 30 mg of the TiO₂ or Pt-TiO₂ catalyst was introduced in the sample cup of the accessory. After enclosure of the catalyst sample with the dome, a flow of 20 mL/min of dry air saturated with ethanol was introduced. After exposure of the catalyst to this flow for 20 minutes, the lines to the cell were closed. A spectrum was recorded of this state of the catalysts after 10 minutes, to evaluate dark reactions, and to serve as background for the series recorded during illumination. The same method was used for propane oxidation, introducing a flow of 20 mL/min of a mixture of 2 vol.% of propane in 19.5 vol.% O₂ into the cell. In-situ IR spectra were recorded every 5 minutes under irradiation. As illumination source a 375 nm LED was used with a maximum light intensity at the catalyst surface of 8 mW/cm².

3. Results

3.1 Catalyst Characterization

Figure 1 shows TEM images of the Pt nanoparticles formed on the calcined Hombikat TiO₂ crystals. The particle size distribution (Figure 1b) indicates that the majority of the particles is of sizes between 1.5 and 3 nm.

Figure 1: (Left) TEM image of Pt particles deposited on TiO₂ crystals and **(right)** the particle size distribution. The lines in the TEM image indicate the size and location of the Pt nanoparticles.

3.2 Propane Oxidation reaction

Before initiating the propane (and ethanol) oxidation experiments, we confirmed that the synthesis procedure of Pt-TiO₂ did not introduce organic residues (of ethylene glycol) on the surface of TiO₂, by exposing the catalyst to 8 mW/cm² in the presence of 19.5 vol.% O₂ for a period of 5 minutes. No significant difference was observed in CO₂ production between unpromoted TiO₂, and Pt-TiO₂. In both cases, the CO₂ concentration was determined to be below 200 ppm.

The increase in CO₂ concentration formed by propane oxidation as a function of time of light exposure, is shown for TiO₂ and Pt-TiO₂ in Figure 2. Except for very minor amounts of CO, the only gas phase product formed is CO₂. Initially, the increase in CO₂ concentration is linear, followed by deviation in linearity when approaching full conversion of propane (after 20 minutes for the TiO₂ sample). Interestingly, TiO₂ is more active than Pt-TiO₂.

Figure 2: CO₂ concentration vs reaction time for standard propane oxidation conditions over TiO₂ and Pt-TiO₂.

In Figure 3 the CO₂ production rates (mmol CO₂/g/hr) are presented as a function of light intensity and oxygen concentration, respectively. Figure 3, left clearly shows that a higher light intensity results in a higher reaction rate. Light intensity thus seems to be the rate determining factor in the oxidation of propane in the range of 0-8 mW/cm², at 19.5 vol.% O₂. Furthermore, the slope in the curves represents the photonic efficiency of the process. Clearly, this efficiency is lower of Pt-TiO₂ than of TiO₂.

Figure 3: CO₂ production rate (r) (**Left**) vs light intensity and (**Right**) vs oxygen concentration in photocatalytic oxidation of propane on TiO₂ and Pt-TiO₂.

The effect of the oxygen concentration (at 8 mW/cm²) is shown in Figure 3, right. For oxygen concentrations increasing between 0-5 vol.%, the reaction rate significantly increases. Increasing oxygen concentration above 5 vol.% has no additional beneficial effect on the reaction rate. The addition of Pt is for all of the oxygen concentrations detrimental to the performance of TiO₂ in propane oxidation.

Finally, the effect of the humidity of the gas phase on catalyst behavior was analyzed, of which the results are summarized in Table 1. Obviously, humidification up to 40% has a negative impact on the photocatalytic performance of both TiO₂ and Pt-TiO₂.

Table 1: Photocatalytic activity of TiO₂ and Pt-TiO₂ for propane oxidation

Catalyst	Reaction rate (dry) (mmol CO ₂ /g/hr)	Reaction rate (40% humidity) (mmol CO ₂ /g/hr)
TiO ₂	3.3	2.0
Pt-TiO ₂	2.5	1.4

3.3 Ethanol Oxidation reaction

The obtained product distributions of the oxidation of ethanol as a function of illumination time are shown in Figure 4. Compared to propane oxidation, there are a number of differences. Whereas for propane predominantly CO₂ is formed, oxidation of ethanol catalyzed by Pt-TiO₂ yields a high gas phase concentration of acetaldehyde, maximizing after 10 minutes. A minor byproduct was observed in the GC analysis. Based on the work of Murcia et al. on ethanol oxidation, we suspect the formation of crotonaldehyde from adsorbed acetaldehyde by β -aldolization and dehydration [11]. The retention time of the unknown product further indicate that, the product is heavier than propane, though less hydrophilic than 2-propanol, in agreement with crotonaldehyde. The consecutive reaction of acetaldehyde to CO₂ can be observed at longer illumination times. Remarkably, the quantities of acetaldehyde and CO₂ produced by un-functionalized TiO₂ are now significantly smaller than of Pt-TiO₂. The addition of Pt thus results in

both a higher acetaldehyde production (rate) during the first 10 minutes, and a significantly higher rate in formation of CO₂.

Figure 4: Concentration of acetaldehyde (Ace) and CO₂ in the photocatalytic oxidation of ethanol over TiO₂ and Pt-TiO₂ at standard conditions versus time.

In Figures 5 the influence of respectively light intensity and oxygen concentration on acetaldehyde and CO₂ production rates are shown, calculated by assuming linearity in the concentration increase in the first 5 minutes of reaction. As can be observed in Figure 5, left, the addition of Pt nanoparticles to TiO₂ has a positive effect on the CO₂ and acetaldehyde production rates for all applied light intensities, the curves indicating a significantly higher photonic efficiency for the platinized catalyst. It should be noted that the higher photonic efficiency implies that the promoting effect of Pt on product formation increases at increasing light intensity. For example, the CO₂ production rate of Pt-TiO₂ is 4.4 times higher than of TiO₂ at 4 mW/cm², and 5.2 times higher at 8.1 mW/cm².

Figure 5: CO₂ and acetaldehyde production rates (r) (**Left**) vs light intensity and (**Right**) vs oxygen concentration in photocatalytic oxidation of ethanol over TiO₂ and Pt-TiO₂.

For un-promoted TiO₂, the effect of oxygen on oxidation rate of ethanol is similar as observed in propane oxidation. There is a strong increase in formation rate, in particular of acetaldehyde, up to an oxygen concentration of 2 vol.%. Oxygen concentrations above 2 vol.% did not result in further increase of rates. For platinized TiO₂, the trends are somewhat different. First, acetaldehyde is formed already at significant rates (1.4 mmol/g_{cat}/hr) in the absence of oxygen. Second, the rate of acetaldehyde production shows a much stronger dependence on oxygen concentration, as compared to the rate of formation of CO₂. The effect of oxygen on acetaldehyde production levels off at 2 vol.% O₂. On the contrary, the rate in CO₂ formation over Pt-TiO₂ is still significantly larger at 10 vol.% as compared to 5 vol.%.

The addition of water vapor to the gas mixture had a small effect on the production rate of CO₂, both for TiO₂ and Pt-TiO₂. The production rate of acetaldehyde was negatively influenced by the addition of water (Table 2).

Table 2: Photocatalytic activity of TiO₂ and Pt-TiO₂ for ethanol oxidation products CO₂ and acetaldehyde

Catalyst	Reaction rate (dry) (mmol CO ₂ /g/hr)	Reaction rate (40% humidity) (mmol CO ₂ /g/hr)	Reaction rate (dry) (mmol ace/g/hr)	Reaction rate (40% humidity) (mmol ace/g/hr)
TiO ₂	0.4	0.6	1.9	1.2
Pt-TiO ₂	1.9	1.8	3.6	3.2

3.4 Combined ethanol and propane oxidation

Oxidation of a binary mixture of propane and ethanol was also analyzed. The propane concentration was fixed at 0.5 vol.%, whereas the ethanol concentration was varied between 0 and 1 vol.%. The results are shown in Figure 6.

Figure 6: CO₂ and acetaldehyde production rates (r) versus ethanol concentration in a gas mixture of ethanol and propane.

In the absence of ethanol, CO₂ is the only reaction product, with the expected higher rate of formation observed for the catalyst without Pt. If the ethanol concentration is increased to 0.2 vol.%, the CO₂ production is increased, which can be ascribed to a contribution to formation of CO₂ of the oxidation of ethanol. Acetaldehyde is not observed at these low ethanol concentrations. However, at an ethanol concentration of 0.4 vol.%, the product distribution completely changes. Acetaldehyde formation is now significant, whereas propane oxidation to CO₂ is significantly suppressed. A further increase in ethanol concentration to 0.9 vol.% finally results in the

same yield in photocatalytic oxidation products as when only ethanol is present, suggesting the absence of any conversion of propane.

3.5 Surface chemistry

The analysis of the chemistry occurring during the oxidation of propane on both the surfaces of TiO_2 and of Pt-TiO_2 is shown in respectively Figures 7, left and right. Whereas in the gas phase only CO_2 is observed, on the surface of TiO_2 carboxylate (likely coordinated formate, inducing spectral features at 1568 ($\nu_a(\text{O-C-O})$), and 1329 cm^{-1} ($\nu_s(\text{O-C-O})$)), and bicarbonate species (at 1420 cm^{-1} ($\nu_s(\text{O-C-O})$)) are formed, in agreement with detailed infrared studies reported in the literature [12, 13]. The sharp band growing in at ~ 1375 cm^{-1} is consistent with the formation of formate ($\delta(\text{CH})$). At longer illumination times, a band grows in at 1713 cm^{-1} . This can be assigned to the ν (C=O) of (H-bonded) formic, and/or acetic acid [16]. The presence of Pt results in a completely different spectrum upon illumination. Carboxylate and carbonate bands are largely absent, whereas absorptions due to carbonyl vibrations, representing (H-bonded) formic or acetic acid ($\nu(\text{C=O})$ at 1712 cm^{-1}) and acetone ($\nu(\text{C=O})$ at 1692 cm^{-1}) dominate the spectrum [12, 13].

Figure 7: DRIFT spectra in the $2000\text{--}1200$ cm^{-1} region obtained between (0–25 min) during oxidation of propane over **(Left)** TiO_2 and **(Right)** Pt-TiO_2

The spectra revealing surface chemistry of TiO_2 and Pt-TiO_2 occurring during photon induced oxidation of ethanol, are shown in Figures 8, left and right,

respectively. Like in the case of propane oxidation, on the surface of TiO₂ several carboxylate species (at 1558, 1352 cm⁻¹) and bicarbonates are formed upon ethanol conversion [12, 13]. The intensities are smaller as observed in the case of propane oxidation, likely due to ethanol stimulated product desorption, to be discussed later. The addition of Pt to TiO₂ again results in the complete absence of the carboxylate and carbonate species. During oxidation of ethanol, two strong bands grow in at 1760 and 1730 cm⁻¹. Given the high initial selectivity to acetaldehyde observed in Figure 5, we assign the band at 1730 cm⁻¹ to acetaldehyde, in good agreement with the data reported in a recent study on photo-oxidation of acetaldehyde [14]. This band potentially shows overlap with the band attributed to (H-bonded) formic or acetic acid at ~1710 cm⁻¹ and the expected broad water bending mode at around 1650 cm⁻¹. The band at 1760 cm⁻¹ is not straightforward to assign. We speculate this is growing in due to ester formation, i.e. due to reaction of the intermediate (hydrogen bonded) formic acid with ethanol, yielding surface bound formyl acetate, HCOOCH₂CH₃. Ester formation has been observed previously by Lin and coworkers [15], when investigating the oxidation reaction of acetic acid on TiO₂.

Figure 8: DRIFT spectra in the 2000-1200 cm⁻¹ region obtained between (0-20 min) during oxidation of ethanol over **(Left)** TiO₂ and **(Right)** Pt-TiO₂

4. Discussion

4.1. Activity and photonic efficiency comparison

To compare the oxidation rates of propane and ethanol, different approaches can be followed. On the basis of reactant, under the applied standard reaction conditions the oxidation rate of propane over TiO_2 is for example 1.1 mmol/g/hr, and of ethanol 2.1 mmol/g/hr. The rate of oxidation of ethanol is thus higher, in agreement with data reported by Zorn et al. [16], who showed for un-promoted TiO_2 that propane oxidation rates are significantly smaller than oxidation rates of 1-propanol. However, to oxidize a hydrocarbon at room temperature by photocatalysis, super oxide anions (O_2^-) are required [17]. These anions are formed by the transfer of an electron from the light activated photocatalyst to an adsorbed oxygen molecule. It is thus useful to also compare the reactions on the basis of oxygen consumption, which is directly relevant for the calculation of the photonic efficiency. By comparing equations (1)-(3), it is obvious that significantly different quantities of oxygen are required to convert the two substrates under consideration. For the production of 1 mol acetaldehyde from ethanol, only 0.5 moles of oxygen is required, significantly less than the 5 moles of oxygen required for the complete oxidation of propane to form CO_2 .

Since the product distributions of propane oxidation or ethanol oxidation are known from experiment, so is the number of converted (activated oxygen) molecules, which is directly corresponding to the number of electrons needed for the respective reactions. To complete the oxidation reaction also a hole scavenger is required, which can be either surface OH-groups, or the reactant molecules adsorbed on the surface. The transfer of

a hole to OH-groups or adsorbed propane as *per* equations (4) or (5), results in the formation of a radical, participating in the reaction.

It currently remains speculation whether the consecutive (radical) oxidation reactions occur on the catalyst surface or in the gas phase. Now, the propane oxidation reaction over TiO₂ consumes 5.5 mmol/g/hr of O₂, and the ethanol oxidation reaction consumes only 1.55 mmol/g/hr of O₂ under standard conditions. Even when the total conversion of ethanol is higher, propane oxidation thus clearly occurs with a much higher photonic efficiency. At the same time, Pt nanoparticles (NPs) induce a slightly negative effect on the CO₂ production rate in propane oxidation, and result in a strongly positive effect on the acetaldehyde and CO₂ production rates in the case of ethanol oxidation. Interestingly, by the addition of Pt NPs, the rate of oxygen consumption in ethanol oxidation (4.65 mmol/g/h) approaches the value calculated for propane oxidation in the absence of Pt NPs (5.5 mmol/g/hr). These oxygen conversion rates can be easily translated in a photonic efficiency, which amounts to approximately 1-2% under standard conditions.

4.2. Relevance of sorption phenomena

The completely different effect of Pt on performance of TiO₂ in oxidation of propane (negative) or ethanol (positive), is likely related to the difference in molecular functionality, and in particular adsorption affinity of propane or ethanol. Ethanol will adsorb strongly on the TiO₂ surface, easily forming ethoxy-groups by reaction with surface hydroxyl groups. Propane on the other hand will adsorb only weakly. Due to this difference, sufficient TiO₂ surface sites are present to activate oxygen for oxidation of propane, whereas in the case of ethanol oxidation, the much smaller quantity of vacant TiO₂ surface sites limits the oxygen conversion rate. The results of the photocatalytic oxidation of a binary mixture of ethanol and propane

(shown in Figure 6) provide additional evidence of the different adsorption strengths of the two substrates. At high ethanol concentrations, by approximation propane is not converted, and reactant (ethanol) selective activity is observed.

The negative effect of water vapor in propane, as well as ethanol oxidation observed for both un-promoted and Pt functionalized TiO_2 is also related to sorption phenomena. Since water competes for surface sites with propane and oxygen (both on TiO_2 and Pt- TiO_2), the negative effect observed in propane oxidation is easily understood, and agrees with observations reported in the literature [18]. Ethanol sorption affinity should however be similar to water adsorption affinity, and the large negative effect is not so easy to explain. Likely, the rate of oxygen activation (in particular over Pt) is reduced by the presence of water, thus diminishing the overall rate. At the same time it appears as if the selectivity to the intermediate product is somewhat diminished, which might be the result of additional formation of hydroxyl radicals by reaction of water with holes, contributing to complete mineralization of ethanol.

4.3. Oxygen activation

The importance of oxygen activation to achieve hydrocarbon conversion, is confirmed by the oxygen concentration dependency of the respective reactions. In propane oxidation, the quantity of super oxide anion radicals is significantly enhanced by increasing oxygen partial pressure, leading to a strong increase in achievable rates, until propane sorption and activation become limiting. The effect of increasing oxygen concentration on the CO_2 production rate by ethanol oxidation over TiO_2 is much less pronounced (Figure 5, right), demonstrating oxygen cannot compete with ethanol for sites.

The positive effect of Pt in ethanol oxidation, is related to the following. First, in agreement with the literature, Pt induces significant conversion of ethanol to acetaldehyde already in the absence of oxygen [11]. The formation of acetaldehyde in the absence of oxygen can be explained by

the dehydrogenation of ethanol over Pt, according to the following reaction:

Second, the addition of Pt nanoparticles provides new sites for oxygen activation. The Pt nanoparticles have a strong affinity for electrons from photo-activated TiO₂ and provide excellent sites for oxygen reduction. Since both ethanol dehydrogenation and oxygen reduction are feasible over Pt, one can speculate that in aerobic conditions, oxidative dehydrogenation of ethanol is a dominant pathway in the formation of acetaldehyde, which we will further discuss in the following.

4.4. Surface selectivity comparison

Besides the above advocated effects of the presence of Pt nanoparticles on the photocatalytic rates of TiO₂, remarkable surface selectivity changes have been observed. The main experimental observations are summarized in Figures 9 and 10. For propane oxidation, carboxylate (formate) and bicarbonate species are dominant on the surface of TiO₂ in the absence of Pt NPs (Figure 9, left), whereas surface bound acetone is the dominant product in the presence of Pt (represented by the gray dots). Gas phase product distributions are comparable (CO₂ and H₂O) for both catalysts. In ethanol oxidation, again carboxylate (formate) and bicarbonate species are dominant species on the surface of TiO₂ in the absence of Pt NPs (Figure 10, left), while acetaldehyde, both on the surface, as well as in the gas phase, is dominant in the presence of Pt NPs. Dotted arrows in Figure 10 indicate relatively slow steps, being O₂ activation and carbonate and carboxylate decomposition in the absence of Pt, and acetaldehyde conversion in the presence of Pt. In both Figures 9 and 10, the purpose is to visualize the effect of Pt nanoparticles on the formation of intermediate species and oxygen activation, and therefore the role of holes receives only limited attention. As described in section 4.1 the holes can either react with adsorbed reactant (in the case of ethanol likely ethoxide), or with surface OH-groups, forming radical species in both cases.

It is remarkable that changes in surface selectivity and gas phase selectivity induced by Pt are comparable in ethanol oxidation, whereas acetone is only observed in large quantities on the surface, and barely detected in the gas phase. We propose that this is again related to the high sorption affinity of ethanol for the surface, stimulating acetaldehyde desorption. A similar 'push-off' mechanism is not applicable for propane oxidation, since propane has less affinity for the surface as compared to the intermediate acetone. It should be noticed that a certain minimum concentration of ethanol is necessary to induce stimulated acetaldehyde desorption, given the low acetaldehyde quantities measured in the gas phase at low ethanol concentration (see Figure 6).

Figure 9: (Left) Propane oxidation over TiO_2 : Carbonates are formed on the surface, while oxygen activation is not inhibited as strongly as in the case of ethanol oxidation. **(Right)** Propane oxidation over Pt-TiO_2 ; Pt changes selectivity to surface bound acetone

Figure 10: (Left) Ethanol oxidation on TiO_2 ; oxygen activation is limited due to blocking of sites by ethanol. Mainly acetaldehyde is formed. **(Right)** Ethanol oxidation over Pt-TiO_2 ; Pt provides oxygen activation sites, resulting in high rates in CO_2 and acetaldehyde production.

To discuss the selectivity differences, the simplified reaction scheme for propane oxidation, presented in Figure 11 is useful. This scheme is based on the study by van der Meulen et al. [13], who used this to explain observed differences in quantities of surface species observed in Rutile or Anatase catalyzed propane oxidation.

Figure 11: Schematic overview of the sequential oxidation steps relevant in propane oxidation. **Top:** Pt-TiO₂, **Bottom:** TiO₂.

The top scheme is the scheme for reaction in the presence of Pt particles, and the bottom scheme in its absence. An identical comparison of schemes can be made for ethanol oxidation, replacing propane for ethanol, and acetone for acetaldehyde (not shown). Bold arrows indicate relatively high rate constants, and 'rds' the rate determining step. The main observation from the experimental DRIFT data when Pt is present, is that formate, and (bi)carbonate are not apparent, while selectively to partially oxidized (surface) products are high. To explain this, our hypothesis is that Pt catalyzes the formation of surface bound acetone (in agreement with acetaldehyde formation in ethanol oxidation), and does not significantly affect the rates of decomposition of formate and (bi)carbonate species to

CO₂. Simply because of the high concentrations of surface bound acetone (or acetaldehyde), formate and (bi)carbonate species are not visible due to limited availability of surface sites. In the absence of the Pt particles it can be hypothesized that formation of surface acetone (or acetaldehyde in ethanol oxidation) is not observed since the oxidation of acetone to carboxylates is faster (and the consecutive oxidation to CO₂ relatively slow (i.e. k_2 is significantly larger than k_3)). The rds in the absence of Pt is the formation of acetone. Observations reported by van der Meulen et al. in comparing rates of different forms of TiO₂ agree with these speculations [13]. Now, the question needs to be answered why Pt predominantly catalyzes oxidation of propane to acetone. The key lies in the activity of Pt-TiO₂ for ethanol dehydrogenation in the absence of oxygen (see Figure 5, right), discussed previously. It can be hypothesized that in the early stages of the photocatalytic oxidation of propane, requiring oxygen, isopropanol is formed. Pt particles are capable of catalyzing dehydrogenation of this intermediate, yielding acetone [19]. Since at the same time, oxygen will be activated over Pt, one can speculate that in fact oxidative dehydrogenation of the intermediate isopropanol to acetone is catalyzed.

As a final point of discussion, the negative effect of Pt particles on the overall oxidation of propane might be related to the formation of large quantities of acetone on the surface of TiO₂: adsorption of propane will be limited by the presence of acetone, thereby lowering the rate (as observed for the absence of propane oxidation in the presence of ethanol, (see Figure 6)). Other potential negative effects of physical origin are currently under investigation [20].

5. Conclusions

The effect of Pt nanoparticles (NPs) on the gas phase photocatalytic oxidation activity of TiO₂ is largely dependent on the molecular functionality of the substrate. We demonstrate that independent of light intensity, Pt nanoparticles decrease rates in photocatalytic oxidation of propane, whereas a strong beneficial effect of Pt was observed in oxidation of

ethanol, both in oxygen lean and oxygen rich conditions. In oxygen lean conditions we attribute the effect of Pt in ethanol oxidation to catalysis in the formation of hydrogen and acetaldehyde. In oxygen rich conditions we propose Pt nanoparticles to provide additional catalytic sites for O₂ reduction, stimulating formation of acetaldehyde by oxidative ethanol dehydrogenation, and consecutive formation of CO₂. Pt nanoparticles result in an increase in oxygen conversion rates from 1.55 mmol/g/hr over TiO₂, to 4.65 mmol/g/hr at a light intensity of 8 mW/cm² at 375 nm. The latter value is comparable to observed for propane oxidation in the absence of Pt, and represents an intrinsic photonic efficiency of the used TiO₂ in the order of 1-2 %.

The large promoting effect of Pt in converting oxygen in ethanol oxidation is related to the strong adsorption of ethanol on the TiO₂ surface, likely forming ethoxy groups, inhibiting oxygen activation over TiO₂. Due to the hydrophobic character of propane, this shows much weaker interaction with the TiO₂ surface, which on the one hand leaves sufficient sites on the TiO₂ surface available for oxygen activation, while on the other hand conversion is significantly suppressed by the presence of hydrophilic species (water, ethanol, and surface bound acetone).

Finally, (surface) selectivity changes induced by Pt are discussed on the basis of the rate determining steps, changing from formation of selectively oxidized (surface bound) products in the absence of Pt, to decomposition of (surface) acetone or acetaldehyde to carboxylates and (bi)carbonates in the presence of Pt.

References

- [1] Y. Paz, Application of TiO₂ photocatalysis for air treatment: Patents' overview, Appl. Catal. B, 99 (2010) 448-460.
- [2] H. Destailats, M. Sleiman, D.P. Sullivan, C. Jacquiod, J. Sablayrolles, L. Molins, Key parameters influencing the performance of

- photocatalytic oxidation (PCO) air purification under realistic indoor conditions, *Appl. Catal. B*, 128 (2012) 159-170.
- [3] M.A. Henderson, A surface science perspective on photocatalysis, *Surf. Sci. Rep.*, 66 (2011) 185-297.
  - [4] M.C. Blount, J.A. Buchholz, J.L. Falconer, Photocatalytic Decomposition of Aliphatic Alcohols, Acids, and Esters, *J. Catal.*, 197 (2001) 303-314.
  - [5] J.J. Murcia, M.C. Hidalgo, J.A. Navío, V. Vaiano, D. Sannino, P. Ciambelli, Cyclohexane photocatalytic oxidation on Pt/TiO₂ catalysts, *Catal. Today*, 209 (2013) 164-169.
  - [6] T. Sano, N. Negishi, K. Uchino, J. Tanaka, S. Matsuzawa, K. Takeuchi, Photocatalytic degradation of gaseous acetaldehyde on TiO₂ with photodeposited metals and metal oxides, *J. Photochem. Photobiol. A*, 160 (2003) 93-98.
  - [7] J.M. Warman, d.H. Matthijs P, P. Pierre, K. Theodorus P.M, v.d.Z.-A. Etty A, M. Adri, C. Ronald, Electronic processes in semiconductor materials studied by nanosecond time-resolved microwave conductivity—III. Al₂O₃, MgO and TiO₂ powders, *Radiat. Phys. Chem.*, 37 (1991) 433-442.
  - [8] J.T. Carneiro, T.J. Savenije, G. Mul, Experimental evidence for electron localization on Au upon photo-activation of Au/anatase catalysts, *Phys. Chem. Chem. Phys.*, 11 (2009) 2708-2714.
  - [9] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, Toward a Physically Sound Structure–Activity Relationship of TiO₂-Based Photocatalysts, *J. Phys. Chem. C*, 114 (2009) 327-332.
  - [10] E. Baranova, T. Amir, P.J. Mercier, B. Patarachao, D. Wang, Y. Page, Single-step polyol synthesis of alloy Pt₇Sn₃ versus bi-phase Pt/SnO_x nano-catalysts of controlled size for ethanol electro-oxidation, *J. Appl. Electrochem.*, 40 (2010) 1767-1777.
  - [11] J.J. Murcia, M.C. Hidalgo, J.A. Navío, V. Vaiano, P. Ciambelli, D. Sannino, Ethanol partial photooxidation on Pt/TiO₂ catalysts as green route for acetaldehyde synthesis, *Catal. Today*, 196 (2012) 101-109.

- [12] A. Mattsson, L. Österlund, Adsorption and Photoinduced Decomposition of Acetone and Acetic Acid on Anatase, Brookite, and Rutile TiO₂ Nanoparticles, *J. Phys. Chem. C*, 114 (2010) 14121-14132.
- [13] T. van der Meulen, A. Mattson, L. Österlund, A comparative study of the photocatalytic oxidation of propane on anatase, rutile, and mixed-phase anatase–rutile TiO₂ nanoparticles: Role of surface intermediates, *J. Catal.*, 251 (2007) 131-144.
- [14] Z. Topalian, B.I. Stefanov, C.G. Granqvist, L. Österlund, Adsorption and photo-oxidation of acetaldehyde on TiO₂ and sulfate-modified TiO₂: Studies by in situ FTIR spectroscopy and micro-kinetic modeling, *J. Catal.*, 307 (2013) 265-274.
- [15] L.-F. Liao, C.-F. Lien, J.-L. Lin, FTIR study of adsorption and photoreactions of acetic acid on TiO₂, *Phys. Chem. Chem. Phys.*, 3 (2001) 3831-3837.
- [16] M.E. Zorn, S.O. Hay, M.A. Anderson, Effect of molecular functionality on the photocatalytic oxidation of gas-phase mixtures, *Appl. Catal. B*, 99 (2010) 420-427.
- [17] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, Photocatalytic purification of volatile organic compounds in indoor air: A literature review, *Atmos. Environ.*, 43 (2009) 2229-2246.
- [18] C.A. Korologos, C.J. Philippopoulos, S.G. Pouloupoulos, The effect of water presence on the photocatalytic oxidation of benzene, toluene, ethylbenzene and m-xylene in the gas-phase, *Atmos. Environ.*, 45 (2011) 7089-7095.
- [19] Q. Gu, X. Fu, X. Wang, S. Chen, D.Y.C. Leung, X. Xie, Photocatalytic reforming of C₃-polyols for H₂ production: Part II. FTIR study on the adsorption and photocatalytic reforming reaction of 2-propanol on Pt/TiO₂, *Appl. Catal. B*, 106 (2011) 689-696.
- [20] R. Su, R. Tiruvalam, A.J. Logsdail, Q. He, C.A. Downing, M.T. Jensen, N. Dimitratos, L. Kesavan, P.P. Wells, R. Bechstein, H.H. Jensen, S. Wendt, C.R.A. Catlow, C.J. Kiely, G.J. Hutchings, F. Besenbacher, Designer Titania-Supported Au–Pd Nanoparticles for Efficient Photocatalytic Hydrogen Production, *ACS Nano*, 8 (2014) 3490-3497.

6

HOW PT CO-CATALYST PARTICLE SIZE INFLUENCES PHOTOCATALYTIC GAS PHASE OXIDATION REACTIONS OVER TiO_2

Abstract

The addition of Pt nanoparticles (1 wt-% loading) induces an intrinsically negative effect on the activity of TiO_2 in the photocatalytic oxidation of propane, which is increasing as a function of increasing particle size from 1.8 to 4 nm. In the oxidation of ethanol, Pt particles with an average size of 1.8 nm show a promoting effect, which decreases as a function of increasing particle size, until at 4 nm the effect is negligible. These results are discussed on the basis of the positive effects of Pt on the efficiency of electron transfer from TiO_2 to O_2 and in oxidative dehydrogenation steps, and the potential negative effect of electron back-donation from Pt to trap states in TiO_2 , which is apparently favored in the case of relatively large particles.

1. Introduction

In the photocatalytic oxidation of organic pollutants by TiO₂ catalysts, the addition of noble metal nanoparticles is often shown to be beneficial [1, 2]. Only in some cases little or negative effects have been reported [1, 3]. The extent of the (positive effect) is often discussed in relation to the size of the noble metal nanoparticles.

Various methods have been used to manipulate the co-catalyst particle size. Hidalgo et al [4] deposited 0.5 wt.% Pt on P25 and Hombikat, and annealed the samples at 100, 300 and 500 °C. Interestingly, the effect of Pt nanoparticles on the activity in liquid phase phenol oxidation was found to be very much dependent on the TiO₂ substrate. Pt negatively affected P25 activity, while positive effects were observed for Hombikat; the highest activity was found for the 300 °C annealed sample. According to Hidalgo et al. [4], the difference in activity between Hombikat and P25 is explained by favorable electron hole separation in P25, due to the presence of an anatase-rutile mixture. Therefore, the addition of Pt is not particularly beneficial. Furthermore, it was shown that there is an optimal particle size, with larger particles becoming detrimental. An explanation for this detrimental effect was not given.

Xing [5] studied the effect of particle size by increasing the loading of Pt from 0.1 to 2 wt.%. The highest activity was obtained for a loading of 0.2 wt.%, which was also the sample with the smallest particle sizes. Other publications also report the highest activity for a Pt loading between 0.5 and 1 wt.% [6, 7], which might be related to the obtained smaller particle sizes at these particle loadings. The effect of particle size was also nicely demonstrated by Zhao et al [6], who compared the effect of sub-nanometer size Pt particles, with those in the range of 1-5 nm, when deposited on P25 TiO₂. For the same loading, the photocatalyst with sub-nanometer particles was clearly more active in both liquid-phase phenol oxidation, and gas-phase NO₂ reduction. The 1-5 nm Pt particles on TiO₂ even resulted in a negative effect on the activity in the phenol oxidation. Zhao et al., however did not provide an explanation for the observed phenomena.

Besides Zhao [6], also Ismael [8] showed that the highest activity was obtained for 0.5 wt.% Pt on TiO_2 , in agreement with the smallest size of the nanoparticles (3 to 15 nm at higher loadings). It should be mentioned that both Zhao and Ismael used a different procedure for the synthesis of the small particles than for the synthesis of the large particles, which might have affected the reactivity of the semiconductor, as was observed for TiO_2 after deposition of Au nanoparticles [1].

A positive effect of small Au co-catalyst nanoparticles was also observed in liquid phase oxidation of 4-chlorophenol [9] and oxalic acid [10]. Iliev [10] et al., showed that smaller particles resulted in a lower adsorption of oxalic acid, up to 50% less in the presence of 5 nm Au particles (1 wt.%) as compared to TiO_2 . Therefore, attention should be paid to possible changes in the surface chemistry and adsorption properties of semiconductors, besides the size of the added nanoparticles contributing to changes in the overall photocatalytic activity.

In summary, as can be observed in Table 1, small particles (1-3 nm) seem to improve co-catalyst properties, although the origin of the effect of these small particles is still unclear. Surface area, the extent of interaction with the semi-conductor, oxidation state, and modification of the semiconductor surface upon metal particle deposition, might all have an effect. Furthermore, it is not well known whether the promoting effect of the metal (Pt) co-catalyst is the result of stimulating oxidation steps (with holes), or reduction reactions (with electrons), and whether in both cases particle size will affect the reaction rate.

Table 1: Summary of articles on particle size effects for photocatalytic oxidation reaction

Author	Particle size (nm)	Loading (wt.%)	Reaction**	Highest activity
Hidalgo [4]	2-3 / 2.5-4 / 4-8	0.5 (Pt)	Phenol (L)	2.5-4nm / 0.5 wt.%
Xing [5]	1-3 *	0.1-2 (Pt)	H ₂ evolution (L)	0.2 wt.%
Zhao [6]	<1 / 1-5	0-2 (Pt)	Phenol (L) / NO ₂ (G)	< 1 nm / 1wt.%
Orlov [9]	3.6-4.8 *	0.5-5 at.% (Au)	4-Chlorophenol (L)	3.6 nm / 0.55 at.%
Iliev [10]	4,5,9,18	1 (Au)	Oxalic acid (L)	5 nm / 1wt.%
Ismael [8]	3 / 15	0.5 (Pt)	Dichloroacetic acid (L)	3 nm / 0.5 wt.%

* Depending on loading, smaller particles for lower loading

** (L) = liquid phase and (G) is gas phase reaction

In chapter 5 we discussed the addition of Pt to calcined Hombikat, which resulted in promotion of photocatalytic activity in ethanol oxidation, and in a (slightly) lower activity in the oxidation of propane. It was proposed that in the ethanol oxidation reaction, the addition of Pt results in new sites for oxygen activation, as well as ethanol dehydrogenation, enhancing the rate. The negative effect of Pt on the rate of propane was tentatively explained by the Pt induced surface selectivity to acetone, inhibiting adsorption of propane and/or O₂ on TiO₂, and thus lowering the reaction rate.

In this work we like to address in more detail the effects of the size of Pt co-catalyst nanoparticles in the inhibition or promotion of the photocatalytic activity in the above mentioned propane or ethanol oxidation reactions. To this end, two different particle sizes of Pt nanoparticles were synthesized via the same wet chemical method, and deposited with the same loading on the TiO₂ photocatalyst. To further study the effect of particle size, both samples were annealed at different elevated temperatures to increase the sizes of the Pt nanoparticles.

2. Experimental set-up

2.1 Catalyst preparation

For the preparation of the Pt loaded photocatalysts, the procedure as described in chapter 5 was used. Commercial Hombikat UV100 (Sachtleben), 100% Anatase TiO_2 , was annealed at 600 °C for 2 hours (heating rate 10 K min⁻¹) in a Joules oven (Carbolite CWF 1100) to obtain a highly active TiO_2 powder [11]. For the preparation of the Pt nanoparticles, first 0.15 M and 0.2 M NaOH ethylene glycol solutions were prepared. The difference in pH between the solutions has been reported to result in different sizes of nanoparticles by Baranova et al. [12]. Chloroplatinic(IV) acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) (Sigma-Aldrich) equivalent to a 1 wt.% loading of Pt, was dissolved in the ethylene glycol solution and heated to 160 °C in a silicon oil bath for 20 minutes. The solution was subsequently cooled to room temperature in a water bath. TiO_2 (500 mg) was suspended in 50 ml mQ water. The suspension was treated for 20 minutes in an ultrasonic bath (VWR Ultrasonic cleaner), after which 80 ml of a 2 M sulfuric acid solution was added drop wise. The cooled solution was added drop wise to the TiO_2 suspension and stirred overnight. The powder was filtered off, and repeatedly washed with mQ water using a centrifuge (Eppendorf Centrifuge 5804), and finally freeze dried.

For the synthesis of the coating, the obtained material was suspended in distilled water and treated in an ultrasonic bath for 30 minutes. The suspension was coated on glass substrates, resulting in 1 mg catalyst per coated sample. The coating was dried under vacuum in a desiccator containing silica gel, before use in photocatalytic experiments.

The photocatalysts loaded with Pt particles synthesized from the 0.15 M and 0.2 M NaOH solutions are called respectively sample 1 and sample 2. After the analysis of catalytic activity of the freshly coated samples, the coatings were annealed at 300 °C. Again after analysis of catalytic activity, the identical coatings were annealed at 500 °C. Besides the coated samples, also some powder was included in the oven treatments, to facilitate TEM analysis after each temperature step.

2.2 Characterization of the catalyst

Transmission Electron Microscope (TEM) measurements were performed using a Philips CM300ST-FEG TEM, and by the use of Noran System Six EDX analyzer Nanotrace detector for verification of the presence of Pt. The TEM pictures were used to determine the particle size by counting of individual particles. Furthermore, XPS analysis was performed to determine the oxidation state of the Pt nanoparticles using a PHI Quantera SMX – XPS system. Five different spots on the sample were analyzed.

2.3 The Photocatalytic reactor system

As is described in chapter 5, the prepared photocatalytic coatings were analyzed in a 2 ml top illuminated batch reactor, equipped with a quartz top window. As illumination source a 375 nm LED was used with a maximum light intensity at the catalyst surface of 8 mW/cm². The reactor was operated in batch mode, after a gas composition was introduced by using a gas flow of 30 ml/min of a predefined mixture obtained by a combination of mass flow controllers (propane and O₂) and liquid evaporation (ethanol and water). After fixed intervals the gas composition was purged into an Agilent 7820 GC system having a Varian CP7584 column and a Methanizer-FID combination for detection.

The O₂ concentration was varied between 0-19.5% and the humidity between 0% and 60%. For propane a concentration of 0.5% was used and for ethanol a concentration of 1.1%. The standard reaction conditions used as reference point in the oxidation reactions were 0.5% propane, 19.5% oxygen, no water vapor, and a light intensity of 8 mW/cm² for a reaction time of 5 minutes. Between different series of measurements, a reaction at reference conditions was performed to ensure that no deactivation occurred. Furthermore, the Pt-TiO₂ catalyst was analyzed for the presence of organic residues from the synthesis by exposing the catalysts to UV-light and synthetic air in the batch reactor, measuring the amount of CO₂ formed and comparing this to the results of unpromoted TiO₂.

The reaction rates were calculated for different light intensities and oxygen concentrations. For the calculations of the reaction rates a reaction time of 5 minutes was used, since this value is still close to the initial rate, while sufficient accuracy is obtained in the detection of CO₂ and/or acetaldehyde.

$$r = \frac{P_{tot} \cdot X_{CO_2} \cdot V}{R \cdot T} \cdot \frac{1}{m} \cdot \frac{60}{t} \quad (1)$$

$$X_{CO_2} = \frac{CO_2 - CO_{2(dark)}}{10^6} \quad (2)$$

The reaction rate, r (mmol/g/hr) of the coating was calculated by equation 1, where P_{tot} is the pressure in the reactor (Pa), V is the volume of the reactor (m³), R the gas constant (m³ Pa/mol K), m the catalyst mass (g) and t the reaction time (min). X_{CO_2} is the fraction of CO₂ of the gas mixture and was calculated by equation 2, where CO_2 is the measured CO₂ concentrations in ppm.

For the ethanol dehydrogenation reaction a fixed reaction mixture of 1.1% ethanol in nitrogen was used. CO₂ concentration measurements were performed after 1.5, 5 and 10 minutes at light intensities between 0-8 mW/cm². The reaction rate was calculated based on the linearity of the increase in CO₂ concentration identified by these 3 measurements, instead of using a single data point obtained after only 5 minutes of reaction, to further enhance the accuracy of the calculated rates.

2.4 In-situ DRIFT spectroscopy

Photocatalytic ethanol and propane oxidation were analyzed by IR spectroscopy using a Bruker Vertex 70 spectrometer equipped with a Liquid N₂ cooled MCT detector, and a Harrick Praying Mantis diffuse reflectance accessory containing a three window cell. One window (Quartz) allowed the illumination of the catalyst formulation with UV/Vis light, while two ZnSe windows provided an optical path for infrared analysis. Prior to the illumination experiments, 30 mg of the Pt-TiO₂ sample 2, not annealed and annealed at 500 °C, catalyst were introduced in the sample cup of the

accessory. After enclosure of the catalyst sample with the dome, a flow of 20 mL/min of dry air saturated with ethanol was introduced. After exposure of the catalyst to this flow for 20 minutes, the lines to the cell were closed. A spectrum was recorded of this state of the catalysts after 10 minutes, to evaluate dark reactions, and to serve as background for the series recorded during illumination. The same method was used for propane oxidation, introducing a flow of 20 mL/min of a mixture of 2 vol.% of propane in 19.5 vol.% O₂ into the cell. In-situ IR spectra were recorded every 5 minutes under irradiation. As illumination source a 375 nm LED was used with a maximum light intensity at the catalyst surface of 8 mW/cm².

3. Results

3.1 Catalyst characterization

The average size and the standard deviation of the Pt particles of sample 1 and 2, when deposited on TiO₂, are shown in Table 2. First of all the difference in pH of the ethylene glycol solution results in smaller particles for sample 1, as expected based on the literature [12].

For both samples annealing results in an increase in the average particle size, while the largest average size is obtained after annealing at 500 °C. By annealing, also the particle size distribution becomes less narrow, as shown in Figure 1. XPS results furthermore showed that the Pt particles on all of the samples were in the Pt⁰ state. Based on the photocatalytic reaction in synthetic air without hydrocarbon substrate (not shown), we can also conclude that the synthesis procedure of the Pt-TiO₂ catalyst did not result in additional residues (of ethylene glycol) on the surface, when compared to the unpromoted TiO₂ sample.

Table 2: Average particle size of samples including number of particles counted between brackets and standard deviation σ .

	Fresh Sample		Annealing at 300 °C		Annealing at 500 °C	
	size	σ	size	σ	size	σ
Sample # 1	1.8 nm	0.5 nm	2.8 nm	0.8 nm	3.8 nm	1.6 nm
	(33)		(50)		(61)	
Sample # 2	2.5 nm	0.8 nm	3.2 nm	1.2 nm	4.1 nm	1.5 nm
	(64)		(61)		(50)	

Figure 1: Particle size distributions (**left**) for the non-annealed samples, (**middle**) for the 300 °C annealed samples and (**right**) for 500 °C annealed samples.

The samples have the following names for simplicity; The fresh sample 1, is 1-25, and the 300 and 500 °C annealed samples respectively 1-300 and 1-500. For sample 2, this is respectively 2-25, 2-300 and 2-500.

3.2 Ethanol dehydrogenation

Ethanol dehydrogenation (in the absence of oxygen) was performed for the fresh Pt-TiO₂ samples 1 and 2 as function of the light intensity and the results are shown in Figure 2. For both samples, besides the main product acetaldehyde only traces of CO₂ were observed. For all light intensities the activity of sample 1 is higher than for sample 2. The sample with the smaller Pt particles (1.8 nm) resulted in a higher activity compared to the larger, 2.5 nm Pt particles in de dehydrogenation reaction.

Figure 2: Rate of Acetaldehyde production in photocatalytic ethanol dehydrogenation versus time for Pt-TiO₂ samples 1 and 2. The photocatalytic experiment was performed in the absence of air.

3.3 Ethanol oxidation reaction

In Figure 3, left and right the effects of respectively light intensity and oxygen concentration are shown. The different catalysts show similar increasing trends in product formation upon increasing light intensity and oxygen concentration. Annealing at 500 °C clearly has a negative effect on the activity of the samples. Intermediate activities were found for samples annealed at intermediate temperatures (not shown).

Figure 3: CO₂ and acetaldehyde production rates (r) (Left) vs light intensity and (Right) vs oxygen concentration in photocatalytic oxidation of ethanol over Pt-TiO₂ sample 1, before and after annealing at 500 °C.

3.4 Propane oxidation reaction

The activity of the different catalysts in the oxidation of propane as function of light intensity and oxygen concentration is shown in respectively Figure 4, left and right. CO₂ is the only product observed in the experiments, besides traces of CO. Pt nanoparticles appear to severely negatively affect the performance of the applied TiO₂ in propane oxidation, and the bigger the particle size of the Pt catalyst is, the lower is the activity of the resulting catalyst. The trend in decreasing activity of the catalytic formulations is identical at variable light intensity and oxygen concentration.

Figure 4: CO₂ production rate (*r*) **(Left)** vs light intensity and **(Right)** vs oxygen concentration in photocatalytic oxidation of propane over fresh Pt-TiO₂ sample 1 and 2 and annealed samples at 300 and 500 °C.

3.5 Surface chemistry

The analysis of the chemistry during the photocatalytic oxidation of ethanol on both the surface of sample 2-25 (Pt25) and sample 2-500 (Pt500) is shown in Figure 5. Two strong bands grow at 1760 and 1729 cm⁻¹ during oxidation of ethanol. In good agreement with the data reported in a recent study on photo-oxidation of acetaldehyde [13], and the selectivity to acetaldehyde observed in Figure 3, we assign the band at 1730 cm⁻¹ to acetaldehyde. The band at 1760 cm⁻¹ we assign to the formation of an ester, likely bound formyl acetate, HCOOCH₂CH₃, as discussed previously in

chapter 5 and proposed by Lin et al. [14]. The comparison of the spectra, shows that the selectivity of the reaction is not significantly altered by the particle size. Comparison of the peak heights as function of time, is in agreement with the difference in activity observed between the small (Pt25) and larger (Pt500) particles.

The spectra of the propane oxidation in Figure 6, show the same trend. The observed peaks at 1712 cm^{-1} and 1691 cm^{-1} can be assigned to carbonyl vibrations, representing (H-bonded) formic or acetic acid ($\nu(\text{C}=\text{O})$ at 1712 cm^{-1}) and acetone ($\nu(\text{C}=\text{O})$ at 1692 cm^{-1}) [15, 16]. No difference in selectivity is observed between 2-25 (Pt25) and 2-500 (Pt-500). In propane oxidation thus no effect of the particle size on the surface chemistry is observed either. Again the trends in growth of peak height confirm the higher activity of the sample containing the smaller particles.

Figure 5: (Left) DRIFT spectra in the $2000\text{--}1500\text{ cm}^{-1}$ region obtained at 30 min after oxidation of ethanol. **(Right)** Peak height at 1729 cm^{-1} as a function of time over Pt 25 and Pt 500.

Figure 6: (Left) DRIFT spectra in the 2000-1500 cm^{-1} region obtained at 30 min after oxidation of propane. **(Right)** Peak height at 1712 cm^{-1} as a function of time over Pt 25 and Pt 500.

3.6 Effect of water vapor

The effect of humidity on the photocatalytic oxidation of ethanol and propane are shown respectively in Figures 7, left and right. Both for samples 1-25 and 1-500 a decrease in activity with increasing water vapor concentration is observed, however the decrease seems less for 1-500. For propane a similar trend is observed in Figure 7, right. However, in this case the water vapor did not affect the activity of the samples annealed at 500 °C and it seems that the larger the Pt particles are, the smaller is the effect of humidity on photocatalytic rates.

Figure 7: CO₂ and/or acetaldehyde production rates (r) versus different relative humidity for the photocatalytic oxidation (**Left**) of ethanol over fresh Pt-TiO₂ sample 1 and 2 and annealed samples at 300 and 500 °C and (**Right**) of propane on fresh Pt-TiO₂ sample 1 and 2 and annealed samples at 300 and 500 °C.

4. Discussion

4.1 Geometrical considerations

The effect of the Pt particle size on the activity was tested for two different reactants (propane and ethanol) and in all cases we observed that the smaller particles resulted in the highest activity of the Pt-TiO₂ samples, as shown in Figure 8, left and right for both oxidation reactions.

Figure 8: CO₂ and/or acetaldehyde production rates (r) versus particle size for the photocatalytic oxidation (**Left**) of propane and (**Right**) of ethanol over Pt-TiO₂.

By including the activity of TiO_2 for both reactions in the figures (indicated by the horizontal lines), some remarkable differences can be observed. First of all, the effect of Pt addition on the propane oxidation rate is negative for all particle sizes. Secondly, in the ethanol oxidation, the effect of Pt is in all cases positive. In the case of the largest particles, the activity is similar to the activity of TiO_2 , and the effect of Pt nanoparticles negligible. The trend in decreasing activity enhancement in the oxidation of ethanol, is in agreement with the observations of Zhao et al. [6]. By increasing the particles size, the surface area of the Pt co-catalyst will decrease, resulting in a lower activity. However, when correcting the observed activity loss (based on oxygen consumption) in ethanol and propane oxidation for Pt co-catalyst surface area, shown in Figure 9, the negative effect on activity is still evident. The oxygen consumption rates are calculated based on the oxygen required to form the measured amount of CO_2 and acetaldehyde and the formed H_2O . The relative rates are calculated by correction of the activity of each sample to the calculated loss of surface area of the Pt nanoparticles using sample 1-25 as reference point, as explained in more detail in the appendix.

Figure 8: Relative oxygen consumption rates for propane and ethanol corrected by the Pt particle surface area based on the average particle size.

Another geometrical consideration has been proposed by Chen et al.[18]. At higher Pt particle sizes, the surface of TiO_2 becomes increasingly covered with Pt, and the number of adsorption sites for the organic reactants decreases. However, the increase in particle size was induced in the work of

Chen by increasing the Pt loading. Since we have used identical loading, and the number of particles is actually decreasing when sintering is induced, such explanation for the activity trends in our study is unlikely. That for propane oxidation in all cases a negative effect is observed, is also inexplicable by geometrical area considerations. Other effects besides loss in area of Pt, or coverage of TiO₂ by Pt particles, need to be considered.

4.2 Catalytic considerations

In the case of hydrophobic propane, weak interactions with the TiO₂ surface can be anticipated, and oxygen activation by in-TiO₂ generated electrons is not limiting the overall rate. For the ethanol oxidation reaction, the strong adsorption of ethanol is limiting the oxygen activation over TiO₂ sites, and Pt provides catalytic centers to achieve oxygen activation, likely the rate determining step. On the basis of oxygen consumption described in chapter 5, a similar activity (and photonic efficiency) as to propane oxidation over TiO₂ is obtained. The increase in Pt particle size will have a negative impact on promoting oxygen reduction in the case of ethanol oxidation.

We have also previously discussed in chapter 5, that Pt dramatically changes the surface selectivity of both reactions, favoring partially oxidized products, compared to carbonate species. Comparing the intermediate products on the surface of both sample 2-25 and 2-500 by DRIFT, no significant difference in surface selectivity is observed. It is therefore highly unlikely that the change in activity of the photocatalysts is the result of changes in surface chemistry, and the differences observed as a function of particle size of the Pt co-catalyst must have an alternative origin.

4.3 Electron transfer phenomena

Since catalytic selectivity is not affected by particle size, and the geometrical losses are insufficient to explain the observed decreasing activity, we suggest that the negative effect is the result of a size dependent competing electron transfer mechanism: back donation of electrons to trap

states of the TiO_2 substrate, rather than electron transfer to oxygen, as shown in Figure 9. It is generally accepted that the electrons formed in TiO_2 are transferred (k_{trans}) to the Pt nanoparticles upon photoexcitation, improving electron hole separation and photonic efficiency. The first option for the in-Pt trapped electrons, is the transfer from the Pt to the reactant O_2 with a certain rate k_{red} . The smaller the Pt particles, the higher the Pt surface area, and therefore the higher the charge transfer rate to adsorbed O_2 likely is. The competing mechanism is illustrated with a certain rate k_{rev} , as described and proposed by Su et al [17]. In the work of Su et al. [17], a shift in base line in the UV-Vis spectrum, during the reduction of methylene blue in an aqueous solution, is used to probe the extent of k_{rev} . Since our work is performed for gas phase reactions, this method to probe the k_{rev} is in our case not directly relevant, and alternative methods, such as Time Resolved Microwave Conductivity measurements, need to be evaluated to determine differences in electron transfer rate as function of Pt particle size.

It is thus currently still speculation how this k_{rev} is possibly linked to the particle size. If particle sizes are small, K_{red} is high, since a large surface area of Pt is available. We could argue that k_{red} is decreasing, due to a smaller reactive surface area, while k_{trans} might not be, or less affected in comparison. When considering a steady state situation, if the electron transfer K_{trans} to the Pt remains equal and the K_{red} is reduced, the only viable option to have a steady state is by an increase of the K_{rev} . That Pt-addition can both have positive and negative effects is also discussed by Emilio et al., based on time-resolved microwave conductivity (TRMC) results [3]. It was argued that multiple phenomena occurred at the same time of which the most important are i) the Pt addition would trap electrons, preventing electron-hole recombination by separation, and ii) that Pt at the same time is helping the recombination of the electrons and holes. This conclusion was based on the experimental observations for Hombikat UV-100, where a significant decrease in the amount of electrons and electron decay time was observed by the addition of Pt. However, only a slight increase in the photocatalytic activity in phenol degradation was observed. The only small increase in activity is not comparable to the significant loss in

electrons transferred from TiO_2 to Pt. The currently most reasonable explanation for this difference is the back donation of electrons via K_{rev} and the resulting recombination. Sun et al [18] have also argued that Pt becomes a recombination center at higher loadings, however no definitive experimental prove was provided by these authors.

Figure 9: Electron transfer mechanisms for platinized TiO_2 , based on a proposal by Su et al. [17]

In Figure 4 we can also observe that the activity of sample 1 is always higher than that of sample 2 for the same annealing temperature. One exception to this rule is the activity of 1-300 compared to the activity of 2-25. The average particle size of 2-25 is smaller than of 1-300, though 1-300 has roughly the same activity. When looking at the particle size distribution, we can observe that the for 2-25 the largest particles are in the range of 3.5 nm, whereas in the case of 1-300 the largest particles are in the range of 4-5 nm. Since both samples also have particles in the range of 1.5-2 nm, it seems that presence of the smallest particles is important and that the loss

of these particles is one of the main causes for a lower observed activity in the case of a larger average particle size.

The addition of water vapor results for both ethanol and propane oxidation in a decrease in activity, as was also observed in chapter 5. However the effect is far more significant for the most active samples with the smallest Pt nanoparticles, whereas the humidity had an only limited effect on the samples annealed at 500 °C. Therefore, it seems that at higher humidity the effect of Pt particle size becomes less relevant, and the adsorption/desorption effects of the substrates induced by the addition of water, become more important. In the case of the 500 °C sample in propane oxidation, the presence of water has no effect, and therefore the negative effect of the particle size is more pronounced than the effect of water.

From these observations we can conclude that first of all the Pt particle size is most relevant under certain (dry) conditions and secondly the promoting effect of Pt in the oxygen activation is counteracted by back transfer of electrons to TiO₂ trap states, which increases with increasing particle size.

5. Conclusions

The size of Pt nanoparticles has a clear and significant influence on the observed activity in both the oxidation of ethanol and propane. For the ethanol reaction the promoting effect of the addition of Pt, increased from almost zero at an average Pt particle size of 4 nm to a more than 2 times higher activity for a particle size of 1.8 nm. For propane the addition of Pt was negative in all cases. At an average particle size of 1.8 nm the negative effect was almost zero and at 4 nm the activity was almost 7 times lower.

The effects of the Pt addition and particle size are explained by the effect of different limitations. For ethanol the limitation of oxygen activation, due to competitive adsorption of ethanol with O₂ for the same sites, is catalytically solved by the addition of Pt, whereas Pt has no effect on the limitations in

the propane reactions. The transfer of electrons from the TiO₂ to the Pt NPs will result in two possible follow-up transfers. The desired transfer is the transfer of electrons from the Pt to oxygen or ethanol, and due to limited transfer capacity, electrons can also be transferred back to TiO₂ traps, which is undesired. Due to their higher surface area, the smaller particles will induce higher transfer rates to adsorbed oxygen, leading to less losses of back transfer, and will thus show higher activities.

References

- [1] S. Oros-Ruiz, J.A. Pedraza-Avella, C. Guzmán, M. Quintana, E. Moctezuma, G. del Angel, R. Gómez, E. Pérez, Effect of Gold Particle Size and Deposition Method on the Photodegradation of 4-Chlorophenol by Au/TiO₂, *Top. Catal.*, 54 (2011) 519-526.
- [2] J.J. Murcia, M.C. Hidalgo, J.A. Navío, J. Araña, J.M. Doña-Rodríguez, Correlation study between photo-degradation and surface adsorption properties of phenol and methyl orange on TiO₂ Vs platinum-supported TiO₂, *Appl. Catal., B*, 150–151 (2014) 107-115.
- [3] C.A. Emilio, M.I. Litter, M. Kunst, M. Bouchard, C. Colbeau-Justin, Phenol Photodegradation on Platinized-TiO₂ Photocatalysts Related to Charge-Carrier Dynamics, *Langmuir*, 22 (2006) 3606-3613.
- [4] M.C. Hidalgo, M. Maicu, J.A. Navío, G. Colón, Photocatalytic properties of surface modified platinised TiO₂: Effects of particle size and structural composition, *Catal. Today*, 129 (2007) 43-49.
- [5] J. Xing, Y.H. Li, H.B. Jiang, Y. Wang, H.G. Yang, The size and valence state effect of Pt on photocatalytic H₂ evolution over platinized TiO₂ photocatalyst, *Int. J. Hydrogen Energy*, 39 (2014) 1237-1242.
- [6] S. Zhao, G. Ramakrishnan, P. Shen, D. Su, A. Orlov, The first experimental demonstration of beneficial effects of sub-nanometer platinum particles for photocatalysis, *Chem. Eng. J.*, 217 (2013) 266-272.

- [7] D. Hufschmidt, D. Bahnemann, J.J. Testa, C.A. Emilio, M.I. Litter, Enhancement of the photocatalytic activity of various TiO₂ materials by platinisation, *J. Photochem. Photobiol., A*, 148 (2002) 223-231.
- [8] A.A. Ismail, D.W. Bahnemann, Mesostructured Pt/TiO₂ Nanocomposites as Highly Active Photocatalysts for the Photooxidation of Dichloroacetic Acid, *J. Phys. Chem. C*, 115 (2011) 5784-5791.
- [9] A. Orlov, D. Jefferson, N. Macleod, R. Lambert, Photocatalytic Properties of TiO₂ Modified with Gold Nanoparticles in the Degradation of 4-Chlorophenol in Aqueous Solution, *Catal. Lett.*, 92 (2004) 41-47.
- [10] V. Iliev, D. Tomova, L. Bilyarska, G. Tyuliev, Influence of the size of gold nanoparticles deposited on TiO₂ upon the photocatalytic destruction of oxalic acid, *J. Mol. Catal. A: Chem.*, 263 (2007) 32-38.
- [11] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, Toward a Physically Sound Structure–Activity Relationship of TiO₂-Based Photocatalysts, *J. Phys. Chem. C*, 114 (2009) 327-332.
- [12] E. Baranova, T. Amir, P.J. Mercier, B. Patarachao, D. Wang, Y. Page, Single-step polyol synthesis of alloy Pt₇Sn₃ versus bi-phase Pt/SnOx nano-catalysts of controlled size for ethanol electro-oxidation, *J Appl Electrochem*, 40 (2010) 1767-1777.
- [13] Z. Topalian, B.I. Stefanov, C.G. Granqvist, L. Österlund, Adsorption and photo-oxidation of acetaldehyde on TiO₂ and sulfate-modified TiO₂: Studies by in situ FTIR spectroscopy and micro-kinetic modeling, *J. Catal.*, 307 (2013) 265-274.
- [14] L.-F. Liao, C.-F. Lien, J.-L. Lin, FTIR study of adsorption and photoreactions of acetic acid on TiO₂, *Phys. Chem. Chem. Phys.*, 3 (2001) 3831-3837.
- [15] T. van der Meulen, A. Mattson, L. Österlund, A comparative study of the photocatalytic oxidation of propane on anatase, rutile, and mixed-phase anatase–rutile TiO₂ nanoparticles: Role of surface intermediates, *J. Catal.*, 251 (2007) 131-144.

- [16] A. Mattsson, L. Österlund, Adsorption and Photoinduced Decomposition of Acetone and Acetic Acid on Anatase, Brookite, and Rutile TiO₂ Nanoparticles, *J. Phys. Chem. C*, 114 (2010) 14121-14132.
- [17] R. Su, R. Tiruvalam, A.J. Logsdail, Q. He, C.A. Downing, M.T. Jensen, N. Dimitratos, L. Kesavan, P.P. Wells, R. Bechstein, H.H. Jensen, S. Wendt, C.R.A. Catlow, C.J. Kiely, G.J. Hutchings, F. Besenbacher, Designer Titania-Supported Au–Pd Nanoparticles for Efficient Photocatalytic Hydrogen Production, *ACS Nano*, 8 (2014) 3490-3497.
- [18] B. Sun, A.V. Vorontsov, P.G. Smirniotis, Role of Platinum Deposited on TiO₂ in Phenol Photocatalytic Oxidation, *Langmuir*, 19 (2003) 3151-3156.

Appendix – Particle size activity correction

The correction of the oxygen consumption rate for the loss of Pt surface area due to the increase in of the particle size is done based on the average Pt particle size of each of the samples. For each sample the volume per particle is calculated assuming spherical particles, and based on an arbitrary volume of 1, the number of particles present are obtained as shown in Table 3. Based on the surface area per particle and the number of particles a total surface area of Pt is obtained. The total surface area for sample 1-25 (1.8 nm, the smallest Pt particle size) is chosen as reference point and based on this value the relative Pt surface area for the other samples is calculated. The oxygen consumption rate is multiplied by the relative surface area of the Pt particles, resulting in a relative oxygen consumption rate as shown in Figure 8.

Table 3: Values for the calculation of the relative surface area of Pt in relation to the average particle size.

particle size (nm)	Volume per particle (nm ³)	Total Volume (nm ³)	Number of particles	Surface per particle (nm ²)	Total Surface (nm ²)	Relative Surface (-)
1.8	3,0	1	0.327	10	3.33	1.00
2.5	8,1	1	0.122	19	2.40	0.72
2.8	11,4	1	0.087	24	2.14	0.64
3.2	17,1	1	0.0582	32	1.88	0.56
3.8	28,7	1	0.0348	45	1.58	0.47
4.1	36,0	1	0.0277	52	1.46	0.44

**CLEAN PREPARATION METHOD FOR THE
SYNTHESIS OF MODEL PHOTOCATALYSTS
LOADED WITH CO-CATALYSTS; SPARK
GENERATOR CHALLENGES**

Abstract

The deposition of clean metal and alloy nanoparticles within a narrow size distribution, without affecting the surface chemical properties of a TiO_2 photocatalyst, can be performed using a spark generator based setup. The spark generated particles are size selected by a differential mobility analyzer (DMA) and deposited on the TiO_2 coating in an electrostatic precipitator. In this work direct deposition without DMA was applied for the deposition of Au, Ag and Pd co-catalysts on Hombikat annealed at 600 °C. Furthermore, attempts to create alloys of these three metals are reported. For the obtained samples, a clear negative effect of Au and Ag was observed on the photocatalytic activity of TiO_2 in the oxidation of propane. On the contrary, AuAg alloy particles did not negatively affect the activity. Therefore, the alloy is expected to induce different relative rates of the various electron transfer steps occurring upon photo-excitation of TiO_2 , as compared to the single phase particles, as discussed in chapter 6 (Figure 9)

In a separate experiment using TiO_2 deposited in a thin film by supersonic cluster beam methodology, DMA size selected deposition results in a homogenous distribution of Au nanoparticles. Agglomeration of the Au nanoparticles was not observed. Further work is required to improve understanding and reproducibility of the deposition of spark generated nanoparticles on substrates, while the spark generator system has potential for preparing model catalyst systems based on nano-alloy co-catalysts.

1. Introduction

Photocatalysis is a promising technology for air purification applications [1, 2]. However for TiO_2 , the mostly used catalyst, currently two major challenges exist. First of all, TiO_2 is only sensitive to UV-light and secondly the relatively high recombination rate of the formed electrons and holes significantly reduces the photonic efficiency of the catalyst [3, 4]. The use of co-catalyst metal nano-particles (NP's) is proposed as one of the solutions to improve electron-hole separation. Electrons are captured by the metal NP's, diminishing efficacy of electron-hole pair recombination [5]. Although indeed in many cases positive effects of metal nanoparticles on photocatalytic activity have been observed [6], we have demonstrated that metal nanoparticles can also have a negative effect on activity, in agreement with literature [7, 8]. It should be noted that comparison of photocatalytic results is challenging. Besides the use of different reactants and reaction conditions, the used synthesis method for nanoparticles, especially in the case of Au, can have a significant effect on the observed activity [9, 10]. To obtain more fundamental insight into the promoting effect of co-catalyst NP's on the photocatalytic activity, clean and well defined synthesis methods for both the catalyst, and the co-catalyst metal NP's are required.

For the synthesis of a clean, active and well-defined TiO_2 coating, Supersonic Cluster Beam Deposition (SCBD) offers a number of advantages [11]. SCBD is a gas phase synthesis method, without the use of any precursor, resulting in a carbon-free TiO_2 surface. Furthermore, the thickness of the coating can be varied [12], high concentrations of dopants can be introduced [13], and by post annealing the desired morphology and crystal structure of the catalyst can be controlled [12, 14, 15], as is described in chapter 3.

For the clean deposition of the co-catalyst nanoparticles, the use of a Spark Generator [16, 17] is highly promising. For the synthesis of the NP's a spark is generated between two electrodes, resulting in a metal vapor cloud. The cloud is strongly diluted and cooled by a high gas flow, in which primary

particles are formed [18]. Due to the (single) charge of the particles, particles can be size selected by an Differential Mobility Analyzer (DMA) and deposited on the TiO_2 coating using an Electrostatic Precipitator (ESP)[19]. This system allows, in theory, the deposition of well-dispersed co-catalyst metal particles of uniform size onto the TiO_2 surface, without altering the surface chemical properties of the catalyst [18]. This method also enables the synthesis of a wide range of alloy nanoparticles [20, 21]. The combination of the SCBD synthesized TiO_2 and the spark generator deposited co-catalysts, minimizes the influence of external factors influencing the promoting effect of the co-catalyst, and therefore enables a more fundamental study of co-catalyst behavior on photocatalytic activity of TiO_2 .

Currently there is only limited experience with deposition of spark generated metal nanoparticles on TiO_2 coatings. Challenges in the deposition of the nanoparticles are for example in the dispersion, particle size and loading of the co-catalysts on the TiO_2 surface. As described in the work of Pfeiffer [18] and Tabrizi [16], after the formation of the small primary particles, these will start to agglomerate, forming larger particles and eventually clusters in the case of sufficiently longer times. The use of the DMA is very beneficial to decrease the particle sizes to the preferred range, however, as a consequence, a majority of the particles produced is excluded, resulting in a significant loss of material.

Besides the ability to deliver narrow particle size distributions of co-catalysts, the spark generator is also able to synthesize alloyed nanoparticles. As described in the work of both Tabrizi [20, 21] and Pfeiffer [18], the alloys can be prepared either via the use of alloyed electrodes, or via the use of a cathode and an anode of a different metals. For the alloyed electrodes this results in particles of which the overall composition is equal to that of the alloyed electrode. In the case of a different anode and cathode, the particles exhibit a distribution of compositions, and the average composition depends on the choice of the metals [20].

In this chapter we address in more detail the effects of the deposition of spark generated particles on prepared coatings of Hombikat annealed at

600 °C (H600), and on well-defined coatings prepared by SCBD. First of all, the potential of direct deposition of co-catalysts for a range of metals and alloys was analyzed. Secondly a deposition of DMA size selected Au nanoparticles on SCBD TiO₂ coatings was performed.

2. Experimental set-up

2.1 Photocatalyst preparation

For the preparation of the H600 coating, Commercial Hombikat UV100 (Sachtleben), 100% Anatase TiO₂, was used as described in Chapter 4. The powder was annealed at 600 °C for 2 hours and when cooled suspended in mQ water and treated in an ultrasonic bath for 30 minutes. By drop casting the TiO₂ suspension was deposited with a loading of 1 mg of catalyst onto a glass plate, and dried under vacuum in a desiccator containing silica gel.

The synthesis of a nanostructured TiO₂ layer was performed by SCBD as described in Chapter 3. Two coatings with a thickness of 400 nm, were deposited on Si-wafer pre-covered with a W-layer. These coatings were used for HR-SEM analysis to determine the distribution and particle size of the deposited co-catalyst particles. The depositions were performed at room temperature and 10⁻² mbar oxygen. After deposition, the coatings were annealed at 500 or 650 °C for two hours (ramp rate 10 K min⁻¹) in a Joules oven (Carbollite CWF 1100).

2.2 Co-Catalyst preparation and deposition

Direct deposition

In the direct deposition system the spark ablation chamber was directly connected to the ESP. Either Ag, Au or Pd rods were used as electrodes. For the formation of the alloys of AuPd and AgPd, the Pd rod electrode was connected to the cathode, and Ag and Au respectively to the anode. For creation of AuAg alloy particles, Au was connected to the cathode, and Ag

to the anode. An inert gas flow of 5 l/min (N_2 , 99.996% purity) was used in cross-flow configuration to flush the 0.5 mm gap between the rods. The nanoparticles were produced by a spark at a voltage of 1.5 kV and a charging current of 0.8 mA. The particles were captured by the ESP with a negative electric field of 7.0 kV for a period of 30 minutes.

Deposition of AgAu alloy and Au using size selection

The size selected deposition of Au was performed with an inert gas flow (Ar, 99.996% purity) continuously flushing the electrode-gap. The Au particles were first carried to size selection in the DMA, and subsequently sent to the ESP for deposition. The experiments were done in cross-flow configuration with a gap distance of about 1 mm between the electrodes. To create size-selected alloy particles, rods consisting of a AuAg alloy (65 wt.% Au) were used, and the procedure was followed similar to the creation of the Au particles. The spark frequency and carrier gas flow rate were kept constant at 60 Hz and 10 l/min for all experiments using a classical RLC circuit. The capacitance was 10 nF and a charging current of 1.14 mA was used. To allow visualization of the generated particles of the AuAg alloy, these were simultaneously deposited on a TEM grid positioned in the corner of the H600 substrates, using the ESP. The deposition of the size selected Au nanoparticles, was performed in a separate experiment on a TEM grid, as well as on the SCBD coating in the ESP. The required deposition time was chosen such, to obtain a loading of approximately 1 wt.% of Au for a coating with an active layer thickness of circa 600 nm.

2.3 Characterization of the catalysts

The metal-loaded TEM-grids were analyzed by a Philips CM300ST-FEG Transmission Electron Microscope to determine the particle size of the as-deposited particles. Furthermore, EDX was used to confirm the deposited metal and alloy ratio of the AuAg particles. The distribution of the Au NP's on the SCBD TiO_2 coating, was analyzed by a Zeiss Merlin HR-SEM via Inlens, and Energy Selective backscatter (ESB) detectors.

2.4 Photocatalytic reactor system

The activity of the samples was measured in the gas phase oxidation of propane and ethanol. The gas mixture used consisted either of 1% ethanol or 0.5 % propane, mixed with 19.5% oxygen diluted in nitrogen. The samples were placed on the bottom of the reactor and illuminated for 5 minutes. For the directly deposited samples, a 375 nm UV led at an intensity of 8 mW/cm² was used. For the SCBD sample, a 365 nm UV-led at an intensity of 25 mW/cm² was used, and a reaction time of 30 minutes was applied. The activity of the coating was analyzed before deposition of the Au NP's, and after the deposition of the Au NP's for comparison. In all cases the product gas was analyzed by an Agilent 7820 GC system having a Varian CP7584 column and a Methanizer-FID combination for detection.

3. Results

3.1 Activity and characterization of co-catalyst directly deposited on H600

For the direct deposition of the spark-generated particles on the H600 surface, in Table 1 the activity is shown for both propane oxidation and ethanol oxidation. Only in the case of the Pd co-catalysts a small increase in activity is observed in propane oxidation. In all the other cases, including ethanol oxidation, the deposition of metal nanoparticles resulted in a (more or less) negative effect. In particular in the oxidation of ethanol the negative effect is remarkable, given the strong positive effect of Pt particles discussed in previous chapters of this thesis.

Two important trends can however be observed. First of all, both Au and Ag co-catalysts particles show a strong negative effect, while if these are combined, the overall co-catalyst effect becomes negligible. Secondly, in the case of the Pd catalysts, alloying with Au or Ag deteriorates activity. In this case the activity appears an average of the activity of either metal.

Table 1: Activity of H600 loaded with range of pure and mixed co-catalysts deposited via spark generator method for both propane and ethanol oxidation reaction using a 375 nm LED (8 mW/cm²).

Sample	CO ₂ (Propane oxidation) (ppm)	CO ₂ (Ethanol oxidation) (ppm)	Acetaldehyde (Ethanol oxidation) (ppm)
TiO ₂	2558	1346	10240
Au-TiO ₂	1227	894	6783
Ag-TiO ₂	1157	702	4260
Pd-TiO ₂	2775	1339	8371
AuPd-TiO ₂	2365	1461	8493
AuAg-TiO ₂	2571	1283	8300
AgPd-TiO ₂	2016	1122	8017

The HR-SEM images of Ag, Au and AuAg on H600, shown in Figure 1, give more insight into the particle size distributions of these formulations. Clear differences between the samples can be observed. For Ag significantly fewer particles are present on the surface, while at the same time the particles are clearly larger in size (around 30 nm). The Au deposition resulted in the highest loading of co-catalysts. For the AuAg samples, the co-catalyst particles were the smallest of the three samples, and the particle density comparable to the Ag sample. Regarding dispersion of the particles, for the Au sample some clustering of particles can be observed on the surface, which was neither the case for Ag nor for AuAg, likely related to the difference in surface density.

Figure 1: HR-SEM images obtained with the ESB detector (**left**) of Ag, (**middle**) of Au and (**right**) of AuAg alloy co-catalyst particle distributions, deposited on H600 coatings.

3.2 AuAg alloy deposition on H600 after size selection

TEM grid images of size selected AuAg alloy nanoparticles are shown in Figure 2. Clearly small particles have been obtained. However on this scale, clearly agglomeration of the primary particles can be observed. Several particles were analyzed by EDX (not shown) for compositional analysis, and in general it was determined that the particles and agglomerates consisted of AuAg alloys, having an uniform composition. The activity of TiO₂ modified by these alloyed particles was also compared before and after deposition, and found to be similar to the AuAg alloy made by the use of two different electrodes, i.e. these particles did not dramatically negatively affect the photocatalytic activity.

Figure 2: Spark generated particles and clusters deposited by electrostatic precipitation on a TEM grid after DMA size selection.

3.3 Size selected deposition of Au on a TEM grid and SCBD coating

Deposition on TEM grid

The deposited Au nanoparticles on the TEM grid are shown in Figure 3. Most of the particles were grain-like shaped with an average length of 6.7 nm. The particles are well distributed over the surface and almost no particles are agglomerated. The particle size distribution is narrow, with

65% of the particles between 6-8 nm size and 80% of the particles between 5-8 nm. Compared to direct deposition shown in Figure 1, the inclusion of the DMA, clearly resulted in a narrow size distribution of smaller and more well-defined Au nanoparticles, which is not possible to achieve otherwise for a spark-based deposition system.

Figure 3: (Left) Well dispersed spark generated Au NP's on a TEM grid, deposited by electrostatic precipitation. **(Right)** The corresponding particle size distribution.

Deposition on the SCBD TiO₂ coating

The results of deposition of Au nanoparticles on the TiO₂ surface are shown in Figure 4. The Au NP's are well distributed over the TiO₂ surface and no agglomeration of particles can be observed. The average size of the particles is roughly 6.5 nm, which is close to the size of the particles deposited on the TEM grid.

Figure 4: HR-SEM image of well dispersed spark generated Au NP on a SCBD deposited TiO_2 layer **(a)** via Inlens and **(b)** via ESB imaging.

The activity of the TiO_2 coated Si-wafers with and without Au particles was also measured. However, as already shown in Chapter 3, the activity of these specific samples is low. A possible activity effect of the Au nanoparticle addition was therefore within the error margin range, and not sufficient to draw any conclusions.

4. Discussion

The deposition of spark generated particles with ESP was performed using three different types of experiments. In the first case, no DMA was used, and particles deposited directly on a H600 coating. The samples produced in this manner, showed clear changes in activity depending on the metal or alloy used. Besides possible intrinsic effects of the metals chosen, the differences can also be due to differences in loading and particle size. For Au, the high loading and the presence of some large agglomerates could explain the reduced activity. For the Ag samples, the smaller size of the alloy particles (fig. 1 right) compared to the pure Ag particles (fig. 1 left) could play a role, but the respective differences in photocatalytic activity are so significant that an effect of the alloying is very probable. It is therefore still speculative but it seems reasonable AgAu shows some synergetic effects, which counteract the negative effects observed for the individually deposited Au and Ag.

It would require deposition of equally sized nanoparticles and clearly defined loadings to be able to perform a more definitive analysis and comparison between the AuAg alloy nanoparticles and its pure metal counter parts. Su et al. [22] confirm the possible benefits of alloys in the form of PdAu core shell particles. In these particles, the ohmic contact properties of Pd are combined with the capacitive properties of Au, resulting in a more active photocatalyst, as compared to the single phase particles. The improved performance is explained by a relatively high electron transfer rate to the reactant (K_{red}), while maintaining a low electron transfer rate back to the photocatalysts (K_{rev}). These electron transfer rates are described in more detail in chapter 6.

The DMA size selected deposition of Au nanoparticles described in section 3.3 showed both for the deposition on the TEM grid as for the deposition on the SCBD TiO_2 layer a good dispersion of the Au particles, no agglomeration and a narrow particle size distribution. Spark generated Au nanoparticles size selected with DMA and deposited on a TiO_2 coating with an ESP therefore have the potential to deliver well defined systems, with Figure 4 as a promising example.

In addition, this method delivers clean nanoparticles within narrow size distributions, without alteration of the surface of the photocatalyst. This enables study of the effects of the nanoparticles on the photocatalytic activity in a more fundamental way than with conventional methods. The versatility of the spark to produce a large range of pure metal and alloy nanoparticles, combined with the deposition of narrow sized nanoparticles, seems highly promising for future research on the effects of co-catalysts properties on the photocatalytic activity. However, currently, due to the relatively low activity of the thin TiO_2 layer on the Si-wafer, it was not possible to measure the effects of the deposition of the Au nanoparticle on the activity with sufficient accuracy. Therefore one of the other main challenges in the development and testing of model catalysts, remains to obtain sufficient activity of thin, well defined photocatalyst layers.

5. Conclusion

To design well defined model catalysts, the combination of SCBD for creation of thin TiO_2 layers with a spark generator system, including a DMA and ESP to generate co-catalyst nanoparticles, is highly promising. The results of the deposition of alloyed AuAg particles suggest an alternative order in relevance of electron transfer steps upon excitation of TiO_2 , given the lower extent of the negative effect on photocatalytic activity of TiO_2 as compared to the single metal particles. Besides the presence of alloy particles, the relative rates of electron transfer steps are also affected by the particle size and/or loading. Further studies with well-defined loadings and narrow particle sizes of nanoparticle co-catalysts are therefore required to affirm intrinsic properties of the alloyed nanoparticles.

The first initial results with DMA combined with ESP show that a good distribution of small Au nanoparticles, deposited on a relatively rough surface of the SCBD TiO_2 coating, with narrow size distribution is possible. However, to analyze the effect of the Spark generated metal and alloy co-catalyst particles, a semiconductor film with sufficient catalytic activity is essential. When achieved, these model catalyst systems will offer a number of opportunities to analyze the effect of a large range of co-catalysts for different and specific reaction environments. Further fundamental understanding of alloyed co-catalysts and co-catalysts in general will become possible, as also the design of photocatalysts for specific processes.

References

- [1] Y. Paz, Application of TiO_2 photocatalysis for air treatment: Patents' overview, *Appl. Catal., B*, 99 (2010) 448-460.
- [2] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, Photocatalytic purification of volatile organic compounds in indoor air: A literature review, *Atmos. Environ.*, 43 (2009) 2229-2246.
- [3] H.H. Mohamed, D.W. Bahnemann, The role of electron transfer in photocatalysis: Fact and fictions, *Appl. Catal., B*, 128 (2012) 91-104.

- [4] L. Zhang, H.H. Mohamed, R. Dillert, D. Bahnemann, Kinetics and mechanisms of charge transfer processes in photocatalytic systems: A review, *J. Photochem. Photobiol., C*, 13 (2012) 263-276.
- [5] A. Naldoni, M. D'Arienzo, M. Altomare, M. Marelli, R. Scotti, F. Morazzoni, E. Selli, V. Dal Santo, Pt and Au/TiO₂ photocatalysts for methanol reforming: Role of metal nanoparticles in tuning charge trapping properties and photoefficiency, *Appl. Catal., B*, 130–131 (2013) 239-248.
- [6] M.A. Henderson, A surface science perspective on photocatalysis, *Surf. Sci. Rep.*, 66 (2011) 185-297.
- [7] M.C. Hidalgo, M. Maicu, J.A. Navío, G. Colón, Photocatalytic properties of surface modified platinised TiO₂: Effects of particle size and structural composition, *Catal. Today*, 129 (2007) 43-49.
- [8] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, The effect of Au on TiO₂ catalyzed selective photocatalytic oxidation of cyclohexane, *J. Photochem. Photobiol., A*, 217 (2011) 326-332.
- [9] W.-C. Li, M. Comotti, F. Schüth, Highly reproducible syntheses of active Au/TiO₂ catalysts for CO oxidation by deposition–precipitation or impregnation, *J. Catal.*, 237 (2006) 190-196.
- [10] G.R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, The influence of the preparation methods on the catalytic activity of platinum and gold supported on TiO₂ for CO oxidation, *Catal. Lett.*, 44 (1997) 83-87.
- [11] B.D. Fraters, E. Cavaliere, G. Mul, L. Gavioli, Synthesis of photocatalytic TiO₂ nano-coatings by supersonic cluster beam deposition, *J. Alloys Compd.*
- [12] F. Della Foglia, T. Losco, P. Piseri, P. Milani, E. Selli, Photocatalytic activity of nanostructured TiO₂ films produced by supersonic cluster beam deposition, *J. Nanopart. Res.*, 11 (2009) 1339-1348.
- [13] M. Chiodi, C.P. Cheney, P. Vilmercati, E. Cavaliere, N. Mannella, H.H. Weitering, L. Gavioli, Enhanced Dopant Solubility and Visible-Light Absorption in Cr–N Codoped TiO₂ Nanoclusters, *J. Phys. Chem. C*, 116 (2011) 311-318.

- [14] A.M. Taurino, S. Capone, A. Boschetti, T. Toccoli, R. Verucchi, A. Pallaoro, P. Siciliano, S. Iannotta, Titanium dioxide thin films prepared by seeded supersonic beams for gas sensing applications, *Sens. Actuators, B*, 100 (2004) 177-184.
- [15] E. Barborini, I.N. Kholmanov, A.M. Conti, P. Piseri, S. Vinati, P. Milani, C. Ducati, Supersonic cluster beam deposition of nanostructured titania, *Eur. Phys. J. D*, 24 (2003) 277-282.
- [16] N.S. Tabrizi, M. Ullmann, V.A. Vons, U. Lafont, A. Schmidt-Ott, Generation of nanoparticles by spark discharge, *J. Nanopart. Res.*, 11 (2009) 315-332.
- [17] B.O. Mueller, M.E. Messing, D.L.J. Engberg, A.M. Jansson, L.I.M. Johansson, S.M. Norlén, N. Tureson, K. Deppert, Review of Spark Discharge Generators for Production of Nanoparticle Aerosols, *Aerosol Sci. Technol.*, 46 (2012) 1256-1270.
- [18] T.V. Pfeiffer, J. Feng, A. Schmidt-Ott, New developments in spark production of nanoparticles, *Adv. Powder Technol.*, 25 (2014) 56-70.
- [19] M.E. Messing, R. Westerström, B.O. Mueller, S. Blomberg, J. Gustafson, J.N. Andersen, E. Lundgren, R. van Rijn, O. Balmes, H. Bluhm, K. Deppert, Generation of Pd Model Catalyst Nanoparticles by Spark Discharge, *J. Phys. Chem. C*, 114 (2010) 9257-9263.
- [20] N.S. Tabrizi, Q. Xu, N.M. van der Pers, U. Lafont, A. Schmidt-Ott, Synthesis of mixed metallic nanoparticles by spark discharge, *J. Nanopart. Res.*, 11 (2009) 1209-1218.
- [21] N.S. Tabrizi, Q. Xu, N.M. van der Pers, A. Schmidt-Ott, Generation of mixed metallic nanoparticles from immiscible metals by spark discharge, *J. Nanopart. Res.*, 12 (2010) 247-259.
- [22] R. Su, R. Tiruvalam, A.J. Logsdail, Q. He, C.A. Downing, M.T. Jensen, N. Dimitratos, L. Kesavan, P.P. Wells, R. Bechstein, H.H. Jensen, S. Wendt, C.R.A. Catlow, C.J. Kiely, G.J. Hutchings, F. Besenbacher, Designer Titania-Supported Au–Pd Nanoparticles for Efficient Photocatalytic Hydrogen Production, *ACS Nano*, 8 (2014) 3490-3497.

DISCUSSION AND OUTLOOK

In this final chapter, the broader implications of the results on the design and applicability of effective devices for gas phase photocatalytic oxidation will be discussed. The focus in this section will be mainly on the results of chapters 4-6. The data obtained for model catalyst systems described in chapter 3 and 7 are of a more fundamental nature, and will be more specifically discussed in section 2, "Outlook".

1.1 Catalyst composition

TiO₂ surface properties

To design effective photocatalytic air purification systems, first a semiconductor of certain morphology has to be chosen. Second, the necessity of a co-catalyst has to be evaluated. In this thesis Hombikat UV-100, a commercially available Anatase TiO₂, was selected as a basis of the investigations. As is shown in Chapter 4, the alteration of this photocatalyst by temperature treatment already significantly affects the behavior of the photocatalyst in gas phase oxidation. Optimized activity under realistic conditions of air purifiers, i.e. 20% oxygen concentration, was obtained after calcination of the Hombikat powder at 600 °C. Therefore, for the studies on co-catalyst effects reported in chapters 5 and 6, Hombikat annealed at 600 °C (H600) was selected. Favorable aspects of this material include particles size (and thus surface area), OH-group concentration, and crystallinity.

Co-catalysts variables

In most of the literature, reporting on the addition of (noble) metal co-catalysts a positive effect on photocatalytic activity is reported, explained by the improvement of electron hole separation. A fair comparison of the results is however rather challenging, due to the use of different photocatalysts, reaction conditions and specific properties of the co-catalysts. The most important parameters that are known to affect the behavior of the co-catalysts are the choice of metal, the particle size, the

loading of the catalyst, and the deposition method used. In this thesis the primary choice of metal was Pt. Pt is seen as one of the most active co-catalysts in general, and one of the most often promising metal co-catalysts in gas phase photocatalysis in particular. Therefore it was anticipated that comparison of our data with literature would be relatively straight forward. In addition, some work in this thesis was done on other metals, to assess the superior behavior of Pt. However, synthesis of particles of these other metals has not been optimized, which makes a comparison between metals on their effects in the photocatalytic conversion of propane and ethanol not possible. Main differences are the particle size, loading and methods of synthesis. Besides the exploratory study on the use of the spark generator, the effect of the synthesis method was not further addressed, and neither the effect of loading. The selected loading of 1% Pt will be further discussed in section 1.3, and the effect of particle size of Pt has received the most significant attention in this thesis.

Understanding effects of Pt-addition

In relation to practical applications, it was demonstrated that small Pt particles had a strong beneficial effect on the conversion of ethanol to both acetaldehyde (undesired) and CO₂ (desired). However, upon increasing particle size in the range from 2 nm to 6 nm, already a significant loss in promotion was observed (Chapter 6). In the case of propane oxidation, the addition of Pt is not beneficial. On the contrary, we observed that the largest particles investigated in the present study induced a strong negative affect on the activity of the applied Hombikat TiO₂, calcined at 600 °C. Whereas electron hole separation might be improved by deposition of Pt nanoparticles, other negative effects of the addition of Pt became in general more significant than the positive contributions of large particles. The positive effect of Pt nanoparticles, in addition to potential physical phenomena, can be assigned to relief of adsorption -desorption limitations. Another observed effect of the Pt was the clear change in surface chemistry both for ethanol and propane as is described in Chapter 5. Surprisingly, while changing the surface chemistry for propane, the small particles did

not result in a significant change in activity of the gas phase CO₂ production. In summary, the usually advocated reasons for the often observed positive effects of the co-catalysts are not so straight forward. Caution is thus required, since the positive effects might not only be related to improved electron hole separation, but also to effects catalytic in nature.

Requirements for comparing co-catalysts

Comparison of different metals as co-catalyst to find the best promoter, would be a great added value. Based on Chapter 6, it can be concluded that it is essential to compare particles of the comparable size, since the same co-catalyst with different particle size, even made by the same synthesis method, can already have a significant, in our case detrimental, effect on the observed activity. For example, some experiments were performed using Au-TiO₂ (not included in this thesis), prepared via wet chemical synthesis and the activity was significantly lower than that of the Pt-loaded samples. Since the particle size was around 20 nm, compared to the 2.5-5 nm of Pt, the difference can either be a result of the choice of metal, or just the particle size.

1.2 Process conditions

Relation to material properties

The results in this thesis and specifically in chapters 4 and 5, show that improving performance is not just merely a task of finding the best semiconductor (TiO₂) and the right co-catalysts. Whereas H0 for example was the best performing catalysts in propane oxidation at low oxygen concentrations, H600 was performing better at 20% oxygen. Furthermore, in chapter 5 it became clear that the addition of Pt was on first sight beneficial in ethanol oxidation, but slightly negative in propane oxidation. In other words, the choice of reactant and reaction conditions are as important as the material properties to define whether a catalyst is actually leading to an improvement or not. The testing of a specific catalyst in only

one set of conditions might thus both result in false positives and false negatives, if not examined in more detail. The results might namely only be applicable for the specific chosen conditions, which are in general not the conditions where the catalyst will be exposed to in practice.

Defining photocatalytic improvement

Definitions of what can be considered as an improved catalyst are also important. The addition of Pt resulted in chapter 5 in an observed higher activity in ethanol oxidation. However when we focused on the oxygen activation/consumption rate of both Pt-TiO₂ and TiO₂, it suddenly became apparent that the addition of Pt was less dramatic as might be anticipated. In this specific case for small Pt-particles, the benefits clearly exceed the negative effects. Analyzing a photocatalyst in an oxidation reaction, requires not only attention on the consumption of reactants, nor only on the formation of products, but also inclusion of the oxygen consumption rates.

Relevance of used reaction conditions

Currently two possible applications are reasonable to consider, namely photocatalytic systems for indoor air quality regulation in homes and offices, and industrial air treatment. Considering the specific conditions used in the experiments presented in this thesis, these are more relevant for industrial applications. The applied concentration levels in house and office air are much lower. However, detecting differences in concentration levels of various contaminants relevant for indoor applications would become challenging. The currently applied GC analysis system would become inaccurate, further limiting the lab testing of household conditions.

The obtained results give insights in the systematics of the catalysts in relation to its process conditions, though for the actual conditions it remains merely speculation how well the system will perform. It is for example questionable, depending on the size of the reactor, if propane at a concentration of a few ppm will actually sufficiently be converted, since the reaction rate at these low concentration, will also be negligible considering

first order reaction rate dependence. Other challenges with the actual conditions are the complex mixtures of organic compounds in real mixtures and the presence of water. In chapter 5 and 6 the presence of water resulted clearly in a lower activity of H600 and Pt-H600. The mixture of propane and ethanol already showed a preferential oxidation, and these are only two components. In this work no experiments are performed with aromatics, acids or other alcohols and alkenes, which is significantly limiting the ability to predict the photocatalytic oxidation behavior in more complex systems.

Long term stability of catalysts

Another factor that was not included in the process conditions was long term testing, to test the stability of the catalysts. The effect of water on the short term for example might be negative, however on the long run it might help to prevent deactivation, and therefore have an overall positive effect. The same effect might also be expected for the co-catalysts addition. The presence of Pt nanoparticles might help to prevent deactivation of the TiO_2 photocatalysts by a change in surface species and ensure a longer and higher activity of the photocatalysts. In the current batch setup, the stability of the photocatalysts was not possible to measure. The catalysts were stable enough to run in multiple set of experiments without deactivation. The only way to measure the stability would be in the form of a continuous reactor for a long period, with regular sampling.

1.3 The photocatalytic frame work

Based on the work presented in this thesis an overview of a number of important system topics influencing the observed photocatalyst performance can be defined as shown in Figure 1. Each of the topics again consists of a number of individual parameters, which are summarized in Table 1. Several of these parameters have been addressed in this thesis. In chapter 3 the initial focus was on the control of the properties of the semiconductor (crystallinity, particle size and porosity) by modifying

synthesis procedures. The focus shifted in chapter 4, to the relation between the photocatalyst and the process conditions for a porous TiO_2 film prepared by wet chemical preparation, without co-catalyst. In chapter 5 the variables of the photocatalyst were kept constant, based on the results in chapter 4, and now process conditions and reactant were varied. In this case an additional parameter was studied by comparing systems with and without Pt nanoparticles. The co-catalyst properties were not changed. In chapters 6 and 7, the focus was further shifted to variation of the co-catalyst. The particle size of Pt nanoparticles was varied in chapter 6, for the same range of process conditions and reactants as used in chapter 5. In chapter 7, more exploratory work was performed to get insight in the possible effects of metal composition (different metals and alloys). Comparison of the spark generated co-catalysts with wet-chemically prepared particles, was however not straight forward due to differences in particle size and loading. In the following the different variables will be discussed in more detail.

Figure 1: Schematic overview of the interaction of the most important variables in a photocatalytic reaction, determining the final activity

Based on the results in this thesis a number of relations between variables within and between different system groups have been identified and discussed. Some on the other hand only received little attention. The effect of temperature is for example not studied in detail. For practical application temperature will in general be less relevant, since most operations will be at room temperature and significant heating and cooling of the gas will have to be avoided. To improve the understanding of adsorption or desorption limitations in relation to the other parameters, temperature on the other hand might be a highly valuable tool for further fundamental study. Within the group of process conditions, reactant concentrations only received relative limited attention in this thesis. During experiments it was however observed that increasing the propane concentration from 0.5% to 2% resulted in an enhanced CO₂ production rate, and the formation of small quantities of acetone. Selectivity changes were also observed in oxidation of ethanol, when the concentration was low. At low ethanol concentrations (<0.2%), ethanol was almost directly converted to CO₂ and significantly less acetaldehyde was observed.

Table 1: Overview of relevant parameters for each of the system groups

Photocatalysts	Process conditions	Co-catalyst	Reactant
Particle size	Reactant concentrations	Particle size	Active groups
Surface area	Oxygen concentration	Metal composition	Intermediates
Crystallinity	Light intensity	Loading	
OH-groups	Humidity	Synthesis method	
	Temperature		

Within the *co-catalyst* system group, only the effect of particle size has been studied in more detail in this thesis. The loading of 1 wt-% Pt was selected based on the literature, in which in general an optimum loading between 0.5-1% was found. In most cases however, the loadings were linked to certain particle sizes. The negative effect observed for Pt nanoparticles might thus be related to the choice of 1 wt-% loading instead of a lower loading. The preparation of TiO₂ catalysts with different Pt wt-% loadings of the same nanoparticle size as is possible with the synthesis

method used in chapters 5 and 6, and would be a relative straight forward way to improve insight on this parameter.

The difference observed between the use of either propane or ethanol as *reactant* in chapter 5 provided valuable insight into the behavior of the photocatalyst. One of the most important variables in this case was the choice of the active groups. Ethanol was hydrophilic (due to the alcohol group) and propane hydrophobic. However, besides the difference of the active group, ethanol and propane also have difference in length (number of C-atoms). Instead of propane, ethane might be seen as a better option for equal comparison. However, i) ethane is probably more stable than propane, and therefore more difficult to oxidize, and ii) more data is already available on propane oxidation, improving the ability to explain observed phenomena in this thesis. The effects of the chain length of the molecule on the reaction rate and selectivity is however not well known and the impact of the choice for propane compared to ethane is recommended for further study. Also conversion of methane, the most stable hydrocarbon, is of interest to evaluate the oxidation potential of photocatalysts. In any case the effect of the active groups of the reactant on the photocatalytic reaction still stands, and by comparing the activity based on oxygen consumption, important conclusions have been drawn. The use of propanol, instead of ethanol, has also been considered. Preliminary experiments showed that the conversion of 2-propanol results in a multitude of products, complicating comparison of activity data significantly, which was not desired.

As already was observed in chapter 5, *competitive adsorption* occurs between the reactants and intermediates. Acetone is more hydrophilic than propane, and therefore was converted to CO₂ before desorption and detection in the gas phase. Due to the strong adsorption of ethanol, the intermediate acetaldehyde was at least partly removed from the surface and detected in significant quantities in the gas phase. Based on the possible oxidation products of a reactant, it is therefore possible to make a first estimation of the gas phase products that might be observed. However

the larger and more complex the compound, the harder it will be to predict the intermediates and oxidation path, as observed for iso-propanol.

2. Outlook

2.1 Model catalysts systems

Table 1 in section 1.3 clearly shows the large number of parameters affecting performance of a photocatalytic system. The results in this thesis show that both process-, as well as catalyst parameters affect the performance of a catalytic coating, and moreover that they are at least partly interdependent. The developed photocatalytic reactor system enabled the use of a large range, well-defined process conditions. However to further unravel the more fundamental aspects of photocatalysts in relation of the process conditions, improvement of the control over the photocatalyst preparation, and functionalization with co-catalyst nanoparticles is essential.

Well defined TiO₂ photocatalysts

The use of commercial Hombikat, and wet-chemical nanoparticle synthesis method, give only limited freedom to control the material properties of the semi-conductor (TiO₂) and nanoparticles. It was therefore that the supersonic cluster beam deposition (SCBD) of TiO₂ and the spark system were explored as alternative methods for obtaining more well-defined and clean photocatalyst systems. The initial results for the SCBD were promising. By studying several synthesis parameters, like introducing oxygen during deposition, annealing of the catalyst, and deposition on glass instead of Si-wafers, significant improvement of the activity was obtained. To further improve the SCBD catalyst coatings, stability of the catalysts should be investigated, as well as a method to define the OH-group concentration of the coatings. Lack of sufficient OH groups has been

identified as one of the causes of the relatively low activity of the layers prepared by SCBD.

Clean and controlled nanoparticle synthesis

For the deposition of co-catalyst nanoparticles, there is a large range of different procedures available. Each metal precursor has its own procedure to achieve the necessary reduction and particle size and often small changes in the applied conditions can result in a different outcome. For alloys it is often even more challenging to find the right method, due to the use of two metal precursors, especially if control over particle size is desired. The use of the spark generator offers the opportunity to i) synthesize co-catalysts of different metals and alloys via the same method, ii) to define a particle size range and iii) to perform deposition without altering the surface by introduction of synthesis residues. The problem of the spark system currently is, that the deposition of the nanoparticles is limited to small, and flat coatings. For large surface area's and three dimensional structures good control over the dispersion of the nanoparticles will be very challenging. Furthermore, for highly porous coatings significant difference in nanoparticle loading between the top and sub-top active layers are likely to occur. The use of thin well defined coatings like made by SCBD, limit the challenges in loading and dispersion, since the top layer on which the co-catalysts is deposited, is thin, and in this case the active layer can be entirely functionalized with nanoparticles. The challenge is to design a system in which an existing photocatalyst powder can be mixed with a co-catalyst particle stream, resulting in a well dispersed deposition. Furthermore, increased rates for the synthesis of defined particles would be essential in such deposition system for powders.

2.2 Path towards photocatalytic gas purification applications

Our laboratory reactor system is designed for quick testing of a large range of photocatalysts in the form of coatings for a range of process conditions. This allows one to get more insight into initial activity and selectivity. For practical applications the current batch design is not suitable, since the capacity is too small to handle large gas flows. To obtain a system suitable for household or industrial application, continuous reactor development is required.

Light distribution in reactor

One of the most important differences between conventional reactors and a photocatalytic reactor is the applied energy source to stimulate the catalytic reaction. Whereas heat can be introduced via transmission to catalysts, light has to be transferred directly to the catalysts, minimizing absorption by the reaction medium as much as possible. The challenge in designing a photocatalytic reactor is therefore in finding a balance between a highly reactive surface area per volume, and the ability to transfer light to the catalysts. The reactor which currently seems to fit the balance between reactive area and light distribution best, is a monolith reactor. In this reactor light can be introduced via fibers. However based on experience, significant losses are present in transferring light from the light sources into the optical fibers. Furthermore, emission along the length of the fiber is often sub-optimal. Optimizing light transfer inside the reactor, and efficient coupling of light into the fiber system can therefore be even more beneficial than further improving the activity of the photocatalyst in perspective of overall efficiency gains. In chapters 3, 4 and 5 it was in all cases observed that light intensity was one of the limiting factors in the reaction rate. Improvement of the photocatalysts, while light intensity is limiting, will, therefore not result in significantly higher conversions. On the other hand, it is also observed, that the photonic efficiency is reduced for higher light intensities, and finding an optimum between photonic efficiency and conversion rates requires further research.

Effects of water and Pt on stability

The development of a continuous system will open-up the ability to analyze the stability of the catalysts. Whereas for the batch experiments reported in this thesis the stability was sufficient (in the order of hours of reaction), for real applications a long term operation stability is essential (few years of operation). In continuous reactors, deactivation of the catalysts can be examined efficiently, and the eventual positive effect of water on stability can be investigated accurately. The same holds true for studying the effect of Pt co-catalysts on the stability of the catalysts. Based on surface chemistry changes by Pt as described in chapter 5, it is expected that the Pt will have a positive effect on the long term stability of the catalysts.

Coating of powder photocatalysts

The current system of coating (on glass substrates) was via drop casting of a water based TiO_2 emulsion. Whereas this coating method might work for flat plate reactors, for other type of reactors it would be required to use an alternative coating technique. Such technique should be able to form homogeneous layers on three dimensional structures, that stick well to the support, so that loss of catalysts during operation is minimized. For the coating of monoliths with TiO_2 one of the few available methods is the use of a sol-gel. The sol-gel can be mixed with powder catalysts, obtaining a coating being a combination of the sol-gel catalyst and the powder catalyst. However, the mixture of the sol-gel and the powder, introduces a possible significant change in the interaction of the powder photocatalyst with the reactants. Furthermore, the sol-gel will have to be annealed, to remove organic residues. This annealing step can also alter the properties of the powder catalyst and also change the particle size of possibly present (noble) metal nanoparticles. It is therefore doubtful, for the current method, to what extent the coating in the monolith represents the photocatalytic powder studied on glass plates in this thesis.

Future household and industrial systems

The reactor design should focus on optimizing light distribution, both for small scale indoor air cleaning systems, as well as for large scale systems to clean industrial gas flows. The requirements for both situations are however completely different. In the case of house hold systems, the composition of the air can strongly fluctuate, requiring a highly flexible system. Furthermore, the photocatalytic system requires most likely incorporation into a large system, to prevent deactivation of the catalysts by dust and inorganic particles, also present in air. The energy consumption for a household module on the other hand is from a consumer's perspective less relevant, since it is expected to be within a reasonable range. However considering gas cleaning on industrial scale of cubic meters per second, requires a significantly larger system and therefore also the energy requirements can make the system economically unattractive. The advantage of industrial gas cleaning on the other hand is that composition is in general stable and a catalyst system for the specific duty can be designed. Overall however, photocatalytic air cleaning systems seems to be most promising and economically applicable for household systems and larger climate control systems.

SUMMARY

Photocatalysis is highly promising as a technology to mitigate environmental pollution. In this thesis the focus will be on air purification by photocatalytic oxidation of volatile organic compounds (VOC's). In **chapter 1**, the basic principles of photocatalysis are introduced. A major challenge in photocatalysis is the low photonic efficiency, due to high electron hole recombination rates. One of the solutions proposed for this issue, is the use of (metal) nanoparticles as co-catalyst. However, currently knowledge on how nanoparticles affect the photocatalytic performance of TiO_2 is limited, especially because of the often complex relation between chosen reaction conditions (light intensity, oxygen and pollutant concentration) and rates obtained for TiO_2 (and co-catalysts). The aim of this thesis is to improve the understanding of the effects of Pt nanoparticles on the rates obtained in photocatalytic oxidation of propane and ethanol over TiO_2 . Control of the properties of TiO_2 and co-catalysts is essential for such fundamental study. Therefore, methods allowing the synthesis of well-defined TiO_2 morphology, and co-catalysts have been used.

In **chapter 2** these methods are explained. The supersonic cluster beam deposition (SCBD) method for the synthesis of thin well-defined TiO_2 layers is described in detail. In this technical chapter also a Spark-generator system is explained, capable of synthesis of well-defined nanoparticles. This system is highly versatile, since nanoparticles, of desired size within a narrow size distribution, can be obtained without contaminations. Furthermore, this method also has the ability to prepare a large range of possible alloys. All samples were analyzed by a homemade photocatalytic evaluation system, which is also described in Chapter 2. A large range of gas vapor mixtures could be prepared and converted with light intensities ranging between 0 and 25 mW/cm^2 . The analysis of the products was performed by a GC-system containing a methanizer and Flame Ionization Detector (FID). Furthermore, Diffuse Reflectance Infrared Fourier Transform

(DRIFT) spectroscopy analysis is described as a tool to complement interpretation of the gas phase catalytic data with the chemistry occurring on the surface of the applied photocatalysts.

In **chapter 3**, model thin layer TiO₂ photocatalysts prepared by SCBD, both on Si-wafer and on quartz glass, are discussed. The method of deposition was optimized by the addition of minor amounts of oxygen during the deposition. The samples could either be annealed during deposition, or afterwards, to obtain crystalline TiO₂ deposits. It was found that annealing at 500 °C resulted in the most active Anatase catalysts. Annealing at 650 and 800 °C resulted in a lower activity. The deposition of TiO₂ layers on a glass substrate resulted in significantly higher activities compared to layers on Si-wafers, and to explain this difference in behavior, it is speculated that the Si-TiO₂ interface stimulates recombination of electrons and holes.

The effects of crystallinity, surface area and quantity of OH-groups of Hombikat on photocatalytic activity, with focus on the applied reaction conditions, are described in **chapter 4**. The Hombikat catalysts were annealed at 200, 400 and 600 °C. For the non-annealed (H0) and annealed samples the activity was analyzed in propane oxidation. The oxygen concentration, propane concentration, and light intensity were varied. The behavior of H0 compared to H600 as function of oxygen concentration was completely different. Whereas for H0, an optimum in activity was found at 2% oxygen, for H600, the highest activity was reached above 10% oxygen. These different dependencies are discussed based on the differences in quantities of OH-groups and crystallinity. On the one hand, a high O₂ concentration is favorable for highly (crystalline) structures of TiO₂, to assure quick consumption of electrons, and to decrease probability of internal charge recombination. On the other hand, for samples with a high OH⁻ surface group density (and relatively low crystallinity), a high O₂ (surface) concentration (>10 vol.%) favors external charge recombination, induced by a relatively low surface propane concentration, and governed by the reaction of superoxide anions with hydroxyl radicals, yielding oxygen and hydroxyl anions.

Hombikat annealed at 600 °C was selected as photocatalyst for further study into the effects of co-catalysts on photocatalytic activity, which are discussed in **chapter 5**. The activity of both TiO₂ and Pt-TiO₂ was tested in the oxidation of ethanol and propane, including mixtures of these compounds, at variable light intensity and oxygen concentrations. The functionalization of TiO₂ with Pt resulted in a significant increase in activity compared to TiO₂ in ethanol oxidation, and in a minor decrease in activity for propane. Comparison of the reactions based on oxygen consumption rates, however, shows that propane oxidation on TiO₂ is most efficient. The addition of Pt improves the oxygen conversion efficiency of the photocatalysts in the oxidation of ethanol, reaching a value close to the value of propane oxidation. The high affinity of ethanol for adsorption on the surface of TiO₂ limits the number of sites for oxygen activation. By the addition of Pt, new oxygen activation sites are created, resulting in an improved activity. The different molecular functionality of propane, resulting in weak adsorption, does not limit oxygen activation, and therefore no beneficial effect of Pt was observed. Based on DRIFT analysis, also a clear effect of Pt on the surface chemistry was observed. The (bi-)carbonate species, mainly observed for both reactions on TiO₂, were not present on the surface of Pt-TiO₂. Instead, the only intermediates on the surface were acetaldehyde and formyl acetate in the case of ethanol oxidation, and acetone and formic and/or acetic acid in the oxidation of propane. It is proposed that the change in selectivity by the addition of Pt is a result of changes in rate limiting steps in the reaction sequence of conversion of the reactants to CO₂.

In **chapter 6**, the effect of the size of the Pt nanoparticles on the photocatalytic activity is studied for both the propane and ethanol oxidation in more detail. Two batches of Pt nanoparticles, with different particle sizes were prepared and deposited on H600 TiO₂. By annealing of the samples at 300 and 500 °C, the particle size was increased, and thus a total of six samples with different Pt particle sizes were obtained. Independent of the reactant, the general trend observed was a decrease in activity with increasing Pt particle size. For ethanol, the overall effect was still positive, due to surface chemical benefits, described in chapter 5

(inhibition of oxygen activation by strongly adsorbing ethanol). The negative effect of larger particle size was not a result of changes in surface chemistry, as confirmed by DRIFT measurements. Furthermore, if corrected for loss in Pt surface area, still an overall negative effect in activity for larger particles in propane oxidation was determined. It is proposed that the negative effect of the addition of Pt, is a result of back-donation of electrons from Pt into TiO₂ trap sites, and that this back donation is more pronounced for larger particles.

Preliminary results of alternative co-catalyst compositions obtained by spark-generation, are described in **chapter 7**. Both H600 coatings, as well as defined SCBD coatings, described in chapter 3, were used as substrates. The direct deposition of Au or Ag on H600 resulted in a drop in activity of the samples in the oxidation of propane, similar to observed for Pt. However the deposition of a mixture of both metals, presumable an alloy, resulted in a much less negative effect in activity. Therefore, the alloy is expected to induce different relative rates of the various electron transfer steps occurring upon photo-excitation of TiO₂, as compared to the single phase particles. Particle size effects and effects of loading could, however, also contribute to the observed phenomena, since these were not exactly similar. To counteract particle sintering and agglomeration, we provide evidence that using a differential mobility analyzer (DMA) and an electrostatic precipitator for deposition of Au nanoparticles, results in a well distributed narrow size range of Au nanoparticles. Further study of alloyed co-catalysts and co-catalysts in well-defined dimensions on photocatalytic activity is recommended.

Finally in **chapter 8**, a more in depth discussion is provided on the implications of the findings of this thesis for practical application of photocatalytic gas phase oxidation to mitigate air pollution. Opportunities for further co-catalysts optimization, considering process conditions encountered in practice, are discussed. Furthermore, in this chapter an outlook is given on how to proceed in the development of commercial gas purification systems, based on photocatalytic oxidation reactors.

SAMENVATTING

Fotokatalyse heeft als technologie veel potentie om milieu vervuiling te reduceren. In dit proefschrift zal de focus voornamelijk gericht zijn op de zuivering van lucht door het verwijderen van vluchtige organische componenten (VOC's). In **hoofdstuk 1** worden de basis principes van fotokatalyse uitgelegd. Een van de grote uitdagingen binnen de fotokatalyse is de lage efficiëntie van de fotonen, door de hoge snelheid van recombinatie van elektronen en gaten. Een van de voorgestelde oplossingen voor dit probleem is het gebruik van (metalen) nanodeeltjes als co-katalysator. De kennis, hoe de nanodeeltjes de fotokatalytische reactie beïnvloeden, is echter op dit moment beperkt, specifiek door de complexe relatie tussen de gekozen reactie omstandigheden (licht intensiteit, zuurstof en reactant concentraties) en de reactiesnelheid van TiO_2 (en co-katalysator). Het doel van deze thesis is om het begrip van het effect van Pt nanodeeltjes op de reactiesnelheden in de fotokatalytische oxidatie van propaan en ethanol over TiO_2 te verbeteren. Goede controle over de eigenschappen van zowel TiO_2 als ook de co-katalysator zijn essentieel voor een dergelijke fundamentele studie. Daarom zijn er synthese methodes gebruikt die resulteerde in een goed gedefinieerde TiO_2 morfologie en co-katalysator.

In **hoofdstuk 2** worden deze methoden uitgelegd. The supersonic cluster beam deposition (SCBD) methode, gebruikt voor de synthese van goed gedefinieerde TiO_2 wordt hier in detail beschreven. In dit technische hoofdstuk wordt ook de Spark-generator opstelling beschreven, waarmee duidelijke definieerde nanodeeltjes gesynthetiseerd kunnen worden. Dit systeem is erg veelzijdig, aangezien hiermee contaminatie vrije nanodeeltjes van een gewenste grootte en met een smalle deeltjesgrootte verdeling geprepareerd kunnen worden. Bovendien, heeft deze methode de mogelijkheid om een zeer breed scala aan gelegeerde deeltjes te synthetiseren, die uit meer dan één metaal bestaan. Alle samples zijn

geanalyseerd met een zelfgemaakte opstelling, beschreven in hoofdstuk 2, om de fotokatalytische activiteit te testen. Een grote variatie aan gas en damp mengsels kon worden bereid en omgezet by licht intensiteiten tussen de 0 en 25 mW/cm². The analyse van de reactieproducten vond plaats met behulp van een GC-systeem doormiddel van een 'methanizer' en een Flame Ionization Detector (FID). Daarnaast wordt ook Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopie beschreven als een methode om the interpretatie van de gas fase data te complementeren met de chemie die plaats vindt op het oppervlak van de gebruikte katalysator.

In **hoofdstuk 3** worden de dunne lagen van TiO₂ als model katalysator bereid met SCBD, zowel op Si-wafer als op kwarts glas bediscussieerd. De depositie methode werd geoptimaliseerd door het toevoegen van kleine hoeveelheden zuurstof tijdens de depositie. De samples konden zowel tijdens als na de depositie worden gecalcineerd om kristallijn TiO₂ te verkrijgen. Het bleek dat calcineren op 500 °C resulteerde in de meest actieve anatase katalysator. Calcinatie op 650 en 800 °C resulteerde in een lagere activiteit. De depositie van een laag TiO₂ op glas als ondergrond resulteerde in een duidelijk hogere activiteit in vergelijking met de TiO₂ lagen op de Si-wafer. We speculeren dat dit verschil verklaard kan worden doordat het Si-TiO₂ grensvlak de recombinatie van elektronen en gaten bevordert.

De effecten van kristalliniteit, oppervlakte en aantal OH-groepen van Hombikat op de fotokatalytische activiteit met de focus op de toegepaste reactiecondities worden beschreven in **hoofdstuk 4**. De Hombikat katalysator werd gecalcineerd op 200, 400 en 600 °C. De activiteit van de niet gecalcineerde (H0) en gecalcineerde samples is getest voor de propaan oxidatie reactie. The zuurstof concentratie, propaan concentratie en licht intensiteit zijn gevarieerd. Het gedrag van H0, in vergelijking met H600 was compleet verschillend als functie van de zuurstof concentratie. De optimale activiteit voor H0 was bij 2% zuurstof, terwijl voor H600 de hoogste activiteit bereikt werd boven de 10% zuurstof. Deze verschillende afhankelijkheden worden besproken aan de hand van de verschillen in OH-groepen en kristalliniteit. Aan de ene kant is een hoge zuurstof concentratie

gunstig voor hoog kristallijne TiO_2 structuren, om er zeker van te zijn dat elektronen snel gevangen worden en hiermee de kans op interne recombinatie sterk wordt verminderd. Aan de ander kant, voor samples met een hoge concentratie OH^- oppervlakte groepen (en relatief lage kristalliniteit), bevordert een hoge (oppervlakte) O_2 concentratie (>10 vol.%) in combinatie met een relatief lage propaan concentratie aan het oppervlak, juist externe recombinatie door een reactie van superoxide anionen met hydroxyl radicalen, resulterende in zuurstof en hydroxyl anionen.

Voor de verdere studie van de effecten van co-katalysatoren op de fotokatalytische activiteit, beschreven in **hoofdstuk 5**, is Hombikat gecalcineerd op 600 °C gekozen als fotokatalysator. De activiteit van zowel TiO_2 en Pt-TiO_2 werd getest voor de oxidatie van propaan en ethanol, inclusief mengsels van beide, voor meerdere licht intensiteiten en zuurstof concentraties. Het aanbrengen van Pt op TiO_2 resulteerde in een significante verbetering in de activiteit in de ethanoloxidatie en in een kleine afname in activiteit in de propaanoxidatie. Vergelijking van de reactiesnelheden op basis van de zuurstof consumptie laat echter zien dat de propaan oxidatie over TiO_2 het meest efficiënt is. De toevoeging van Pt verbetert de zuurstof omzettingsefficiëntie van de fotokatalysator in de ethanol oxidatie tot waardes die in de buurt komen van de propaan oxidatie. De hoge absorptie affiniteit van ethanol met het TiO_2 oppervlak limiteert het aantal mogelijke 'sites' voor zuurstof activatie. Door de toevoeging van Pt worden nieuwe actieve sites gecreëerd, dat resulteert in een verbeterde activiteit. Het verschil in moleculaire functionaliteit van propaan met als resultaat een zwak absorptie maakt dat zuurstof activering niet limiterend is en hierdoor wordt er voor Pt in deze situatie geen positief effect waargenomen. In de DRIFT analyse is ook een duidelijk effect van Pt op de oppervlakte chemie waargenomen. De (bi-)carbonaat groepen, voornamelijk waargenomen in beide reacties op TiO_2 , zijn niet aanwezig op het oppervlak van Pt-TiO_2 . In plaats daarvan zijn op het oppervlak, alleen de tussenproducten acetaldehyde en formyl acetaat in het geval van ethanol, en aceton en mierenzuur en/of azijnzuur in de propaan oxidatie waargenomen. Het is voorgesteld dat de verandering in selectiviteit door de

toevoeging van Pt een gevolg is van een verandering in de snelheidsbepalende stap in de opeenvolgende reactie stappen voor de omzetting van de reactant naar CO₂.

In **hoofdstuk 6**, is in meer detail het effect van de grootte van de Pt nanodeeltjes op de fotokatalytische activiteit voor zowel de propaan en ethanol oxidatie bestudeerd. Twee batches van Pt nanodeeltjes, met verschillende deeltjes grootte zijn bereid en aangebracht op H600 TiO₂. Door calcinatie van de samples op 300 en 500 °C, zijn de deeltjes groter gemaakt en op deze manier is een totaal van zes samples met verschillende deeltjes groottes verkregen. Onafhankelijk van de reactant is de algemeen waargenomen trend, dat de activiteit afneemt met de toename in deeltjes grootte van Pt. Voor ethanol was het effect nog steeds positief, door de oppervlakte chemie als is beschreven in hoofdstuk 5 (limitering van zuurstof activatie door sterk geabsorbeerd ethanol). Het negatieve effect van grotere deeltjes was geen gevolg van een verandering in oppervlakte chemie, hetgeen door DRIFT meting wordt onderschreven. Bovendien, wanneer gecorrigeerd voor het verlies in oppervlakte van Pt, wordt er nog steeds een negatief effect waargenomen voor grotere deeltjes in de propaan oxidatie. Het is voorgesteld dat het negatieve effect van de toevoeging van Pt een gevolg is van de terug-donatie van elektronen van Pt naar TiO₂ 'trap sites' en dat dit effect sterker is voor grotere deeltjes.

De voorlopige resultaten van de alternatieve co-katalysator samenstellingen verkregen via spark-generation worden beschreven in **hoofdstuk 7**. Zowel H600 lagen, als ook goed gedefinieerde SCBD lagen, beschreven in hoofdstuk 3 zijn gebruikt als substraat. De directe depositie van Au of Ag op H600 resulteerde in een afname in de activiteit van de samples in de oxidatie van propaan, vergelijkbaar als is waargenomen voor Pt. Echter de depositie van een mengsel van beide metalen, waarschijnlijk een legering, had een veel minder negatief effect op de activiteit tot gevolg. Daarom wordt er verwacht dat de legering andere relatieve snelheden van de verschillende elektron overdracht stappen induceert tijdens foto-excitatie van TiO₂, in vergelijking met de deeltjes, die uit één metaal bestaan. Echter, aangezien deeltjes grootte effecten en belading niet exact

hetzelfde waren voor de verschillende samples, kunnen deze ook de oorzaak zijn voor de waargenomen effecten. Om het sinteren van deeltjes en agglomeratie tegen te gaan, laten we zien dat het gebruik van een differential mobility analyzer (DMA) en een electrostatic precipitator (ESP) voor de depositie van Au nanodeeltjes, resulteren in een goede distributie van de aangebrachte Au nanodeeltjes met een kleine deeltjes grootte verdeling. Verdere studie naar het effect van gelegeerde deeltjes en naar co-katalysatoren met duidelijk gedefinieerde dimensies op de fotokatalytische activiteit wordt aangeraden.

Tot slot in **hoofdstuk 8** wordt er voorzien in een meer diepgaande discussie over de implicaties van de bevindingen in dit proefschrift op de praktische toepassing van fotokatalytische gasfase oxidatie om lucht vervuiling te verminderen. Mogelijkheden voor verdere verbetering van co-katalysatoren met praktische proces condities in overweging genomen, worden besproken. Daarnaast wordt er in dit hoofdstuk een toekomstperspectief gegeven voor de vervolg stappen die genomen moeten worden in de ontwikkeling van een commercieel gaszuiveringssysteem, gebaseerd op fotokatalytische oxidatie reactoren.

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