



Evaluating silica gel supported titanium dioxide for use as a photocatalyst
by Michael Owen Hardiman

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
© Copyright by Michael Owen Hardiman (2001)

Abstract:

With increasing attention given to the clean up of polluted waters, new technologies need to be developed to offer safer, cheaper methods than those currently employed. Most current systems employ oxidizing agents which are costly, consumed in the process and often hazardous to work with. The use of titanium dioxide as a photocatalyst offers a safe alternative to current technologies and has been proven to degrade a wide number of contaminants. The majority of recent work in photocatalysis uses titanium dioxide slurry type reactors and separation is required to reclaim the catalyst. This will limit the applicability of this method due to the added separation expense. Supporting titanium dioxide for use in a packed bed configuration represents a viable alternative. Experiments were developed for the evaluation of supported titanium dioxide as a photocatalyst. Silica gel was chosen as a support material due to its unique properties regarding UV transmission, surface area and adsorptive capability for water and organics. The support materials were optimized for light transmission properties with respect to manufacturer, grade and size fraction. Coating methods were developed, and four continuous flow, annular reactors were designed to evaluate the supported photocatalysts. Through light measurements and kinetic experiments, four supported catalysts were evaluated in the four reactors for their ability to degrade formic acid. The degradation rates observed with the supported catalysts were found to have a strong dependence on catalyst loading and support material, but nonetheless outperformed slurry catalysts under identical conditions.

EVALUATING SILICA GEL SUPPORTED TITANIUM
DIOXIDE FOR USE AS A PHOTOCATALYST

by

Michael Owen Hardiman

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

of

Master of Science

in

Chemical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

December 2001

N 378
H 2149

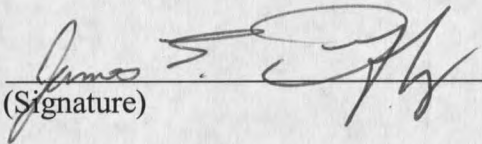
APPROVAL

of a thesis submitted by

Michael Owen Hardiman

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

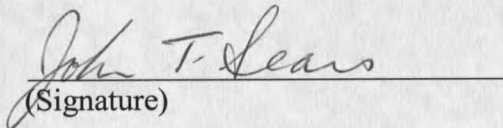
Dr. James Duffy


(Signature)

01-10-02
(Date)

Approved for the Department of Chemical Engineering

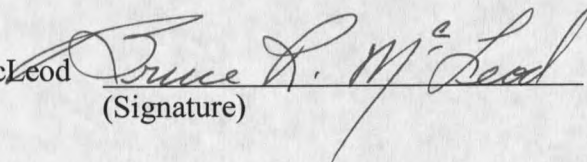
Dr. John Sears


(Signature)

01-10-02
(Date)

Approved for the College of Graduate Studies

Dr. Bruce McLeod


(Signature)


1-14-01
(Date)

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under the rules of the library.

If I have indicated my intentions to copyright this thesis by including a copyright notice page, copying is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for permission for extended quotation from or reproduction of this thesis in whole or in part may be granted only by the copyright holder.

Signature

A handwritten signature in black ink, appearing to be "M. D. R.", written over a horizontal line.

Date

12/4/01

TABLE OF CONTENTS

1. INTRODUCTION AND BACKGROUND.....	1
Photocatalysis and Photocatalysts.....	3
Titanium Dioxide.....	5
Titania Surface.....	5
Mechanisms for Heterogeneous Photocatalysis using TiO_2	8
Catalyst Supports.....	11
Silica Gel.....	15
Photoreactors.....	16
Radiant Flux.....	18
Statement of Objectives.....	20
2. EXPERIMENTAL METHODS AND MATERIALS.....	22
Catalyst Supports.....	22
Light Penetration Tests.....	23
P25 TiO_2 Catalysts.....	25
TiO_2 Assay.....	26
Annular Reactors.....	26
Reaction Runs.....	29
Slurry Runs.....	30
Sample Analysis.....	31
3. RESULTS AND DISCUSSION.....	32
Choosing the Support Material.....	32
Light Penetration Through Annular Spaces.....	35
Coatings.....	36
Formic Acid Runs.....	37
Packed Bed Annular Reactor Runs.....	41
Slurry Runs.....	46
Data Analysis.....	49
Volume Correction.....	49
Normalization to Rate of Energy Absorbed.....	52
SEM.....	58
Conclusion.....	60
Future Work.....	62

TABLE OF CONTENTS - CONTINUED

REFERENCES CITED.....	63
APPENDICES.....	65
APPENDIX A.....	66
Formic Acid Runs Data.....	67
APPENDIX B.....	74
Spectrophotometric Method for the Determination of TiO ₂ Loading.....	75

LIST OF TABLES

Table	Page
1. Support Materials Used According to Size Fraction and Manufacturer.....	22
2. BET Data of the Silica Gels Used.....	23
3. Annular Reactor Dimensions.....	27
4. Five Consecutive Runs in 2.0" Reactor with 0.4 Weight Percent P25 on Grade 58.....	40
5. Summary of Supported and Suspended Observed Rates.....	48
6. Volume Corrected Rate Constants for the Various Catalysts.....	51
7. System Specific Extinction Coefficients.....	54
8. Summary of Intensity Normalized Rate Constants for the Various Catalysts.....	55
9. Comparison of Spectrophotometric and ICP-AS Methods.....	76

LIST OF FIGURES

Figure	Page
1. Charge Separation in a Semiconductor Particle Upon Excitation with Light.....	4
2. Surface Hydroxyl Groups on Titania.....	6
3. Photodegradation Rate Dependence on Radiant Flux.....	19
4. Acrylic Box Used in Support Material Light Penetration Tests.....	24
5. Light Intensity Measurements in Packed Annular Reactors.....	25
6. Annular Photoreactor.....	28
7. Schematic of Experimental Photoreactor Setup.....	29
8. Light Transmission Through Grade 58 Silica Gel and Borosilicate Glass Beads.....	32
9. Light Penetration Through Different Brands of 12-18 Mesh Silica.....	33
10. Light Penetration Through Various Size Fraction of Grade 58 Silica Gel.....	34
11. Comparison of Light Penetration Through Coated and Uncoated Silica.....	35
12. Light Penetration Through Annular Reactors Packed with Coated and Uncoated Silica.....	36
13. 2.00" Reactor Packed with 0.4 Weight Percent P25 on Grade 58 Silica.....	39
14. 2.0" Reactor Packed with 0.4 Weight Percent P25 on Grade 58 Silica at Varying Flow Rates.....	40
15. Observed Rate Versus Mass TiO_2 in Annular Reactors Packed with 0.4 Weight Percent P25 on Grade 58 Silica.....	41

LIST OF FIGURES - CONTINUED

Figure	Page
16. Observed Rate Versus Mass TiO_2 in Annular Reactors Packed with 0.04 Weight Percent P25 on Grade 58 Silica.....	42
17. Comparison of Grade 58 and Grade 55 Silica Gels.....	43
18. Light Penetration Tests with Uncoated 12-18 Mesh Silica Gel.....	44
19. Comparison of Observed Rates Versus Mass of Titania for the Various Catalysts.....	45
20. Comparison of Observed Rates with Supported and Suspended P25 Titania.....	47
21. Experimental Photoreactor System.....	50
22. Light Measurements for Intensity Balance on Photoreactors.....	53
23. Linearization of Equation 32 with Experimental Data to Give b Terms.....	54
24. Radial Dependence of k_{IC}	58
25. SEM of Silica Gel Particles.....	59

ABSTRACT

With increasing attention given to the clean up of polluted waters, new technologies need to be developed to offer safer, cheaper methods than those currently employed. Most current systems employ oxidizing agents which are costly, consumed in the process and often hazardous to work with. The use of titanium dioxide as a photocatalyst offers a safe alternative to current technologies and has been proven to degrade a wide number of contaminants. The majority of recent work in photocatalysis uses titanium dioxide slurry type reactors and separation is required to reclaim the catalyst. This will limit the applicability of this method due to the added separation expense. Supporting titanium dioxide for use in a packed bed configuration represents a viable alternative. Experiments were developed for the evaluation of supported titanium dioxide as a photocatalyst. Silica gel was chosen as a support material due to its unique properties regarding UV transmission, surface area and adsorptive capability for water and organics. The support materials were optimized for light transmission properties with respect to manufacturer, grade and size fraction. Coating methods were developed, and four continuous flow, annular reactors were designed to evaluate the supported photocatalysts. Through light measurements and kinetic experiments, four supported catalysts were evaluated in the four reactors for their ability to degrade formic acid. The degradation rates observed with the supported catalysts were found to have a strong dependence on catalyst loading and support material, but nonetheless outperformed slurry catalysts under identical conditions.

CHAPTER 1

INTRODUCTION AND BACKGROUND

This past century has seen a rapid increase in pollutants in our environment. Toxic pollutants in the soil, air and water are widespread. Continual human contact with toxins and the steady degradation of the environment is a growing concern on national and international agendas. The sources of these contaminants are extensive, ranging from (but not limited to) the chemical/petroleum industries, textiles, pulp and paper milling to increases in modern agriculture practices.

A considerable amount of research is currently being directed towards improving methods of contaminant treatment. Current processes in use such as air stripping or activated carbon adsorption offer only a phase change of the contaminant, likely requiring further treatment. Other methods, such as treatment with a strong oxidant (e.g. ozone or chlorine), generally offer less than complete removal of organic contaminants while consuming large quantities oxidants. Relatively new to the arena are methods collectively termed advanced oxidation processes (AOP's). These methods may be cheaper and offer better degradation than some of the above-mentioned methods. Examples of AOP's include direct UV photolysis of the contaminant, UV/ozone or UV/H₂O₂, and heterogeneous photocatalysis. The latter three of the these processes are of particular interest in that they have shown potential to kill bacteria as well as degrade organic compounds (1). Direct photolysis of an organic contaminant requires that it absorb the incident light and suffer degradation as a result. This is difficult to achieve

with most contaminants, especially at the low concentrations generally encountered in waste treatment. UV/ozone and UV/H₂O₂ have shown promise as effective treatment methods. When UV is used in conjunction with ozone or hydrogen peroxide, highly reactive hydroxyl ([•]OH) radicals are generated, which will non-selectively attack most organic compounds. While complete degradation is possible with these methods, large amounts of oxidant are consumed in the process. On the contrary, in heterogeneous photocatalysis reactive radicals (thought to be primarily [•]OH radicals) are generated *in situ* from air, oxygen or water (2) without the need for costlier and more hazardous oxidizers. In heterogeneous photocatalysis, a solid photocatalyst (usually an n-type semiconductor such as TiO₂, ZnO, or CdS) is illuminated with UV-visible light creating a reduction-oxidation (redox) environment (to be described in more detail later) that has been shown to be capable (3) of degrading a wide variety of organic contaminants. Other features that make heterogeneous photocatalysis attractive is that it generally uses low cost, non-toxic catalysts, can often be operated at ambient conditions and is capable of absorbing a wider portion of the UV spectrum efficiently as compared to other UV methods (2). In addition to air, water and wastewater treatment, heterogeneous photocatalysis has been used for a wide range of reactions including: mild organic oxidations, dehydrogenation, hydrogen transfer, O₂¹⁸-O₂¹⁶ and deuterium-alkane isotopic exchange, and metal deposition (4). Heterogeneous photocatalysis has been confirmed by numerous researchers to be effective for the total oxidation of organic water contaminants (5).

Photocatalysis and Photocatalysts

Though there is currently some dispute as to a proper definition of photocatalysis, a general definition is the “acceleration of a photoreaction by the presence of a catalyst”

(3). For the purpose of water treatment, heterogeneous photocatalysis can be loosely defined as the illumination of a particulate with UV-visible light of suitable energy to initiate redox chemistries (1) while the catalyst itself undergoes no overall change.

Semiconductors have largely been employed for use as photocatalysts because of their electronic structure, light absorption properties, charge transport characteristics, and excited state lifetimes (3). A detailed description of semiconductor materials is beyond the scope of this thesis and only some of the properties applicable to photocatalysis will be addressed. For a more complete treatment see Reference 6.

A semiconductor is characterized by a filled valence band and an empty conduction band. For a semiconductor material to be used as a photocatalyst, an excited state must be induced in the material by the absorption of light. Upon excitation by the absorption of a photon of sufficient energy, charge separation takes place as an electron (e^-) is promoted from the valence band to the conduction band. The absence of an electron in the valence band (or a positive charge) is known as a hole (h^+). The act of excitation by light is determined by the band gap, or the energy gap, between the valence and the conduction band energy levels. For promotion of an electron to occur, the photon energy must exceed the energy of the band gap.

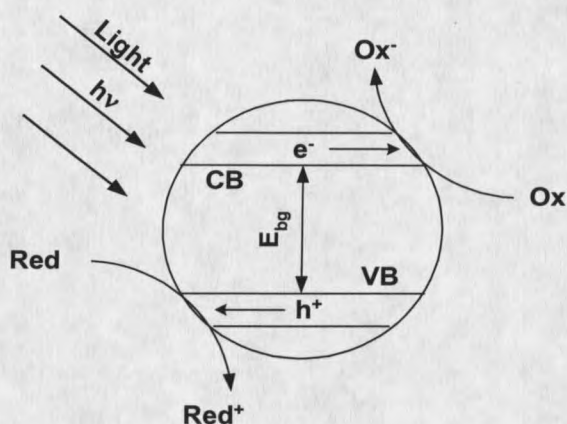


Figure 1. Charge separation in a semiconductor particle upon excitation with light ($h\nu > E_{bg}$). Ox and Red are oxidant (electron acceptor) and reductant (electron donor) respectively.

The existence of the band gap prevents rapid recombination (or deactivation of the excited state) of the electron-hole pairs (3). In the excited state, the electron and hole pairs will either recombine or diffuse to the surface of the semiconductor where they can participate in charge transfer reactions, though certain conditions must exist at the surface for this to occur. From Gratzel (3), "For semiconductor particles dispersed in a gaseous, liquid, or solid medium, the charge transfer can take place only in the presence of an electroactive species acting as electron donor or acceptor. Thus an interfacial redox reaction is required to produce the electric field within the particle". Species on the surface of semiconductors act as traps for the electrons and holes and prevent their recombination, allowing charge transfer to take place. For heterogeneous photocatalysis in the treatment of water, the electron donors and acceptors are mainly in the form of adsorbed oxygen and water molecules or surface bound hydroxyls (this to be treated in greater detail later).

Titanium Dioxide

In the area of water and wastewater treatment, the principal focus has been on the use of titanium dioxide or titania (TiO_2) as a photocatalyst. Mills and Le Hunte (7) proposed the following list of criteria in choosing a semiconductor for use as a photocatalyst:

1. Photoactive.
2. Able to utilize visible and/or near UV light.
3. Biologically and chemically inert.
4. Photostable (i.e. not liable to photoanodic corrosion for example).
5. Inexpensive.

Titania meets these criteria well and has been shown to exhibit a high photoactivity towards a wide range of compounds (7, 8). TiO_2 requires light less than 390 nm to be photoactive and has been shown to be capable of using sunlight to degrade organic pollutants (3). Approximately 4-6 % of the available sunlight (the amount of sunlight in the 300-390 nm wavelength region) has been demonstrated to initiate the photoactivity of titania (6).

Titania surface

In an aqueous environment, the surface of titania will be covered with hydroxyl groups. The extent of this coverage will depend on crystal phase and preparation conditions. The point of zero charge (PZC) of TiO_2 used in photocatalysis is in the pH range of 6-7 (3), with the surface positively charged in acidic environments. Titania is known to exist in three different crystal phases: anatase, rutile, and brookite.

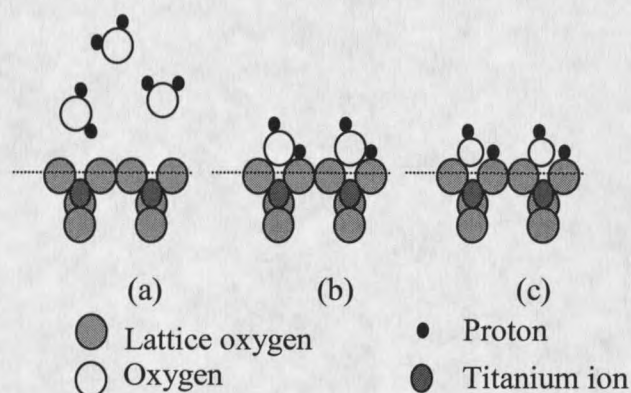


Figure 2. Surface hydroxyl groups on titania (17). (a) hydroxyl free surface; (b) physical adsorption of water; (c) dissociation of water, giving two distinct OH⁻ groups.

The annealing conditions will determine the crystal structure. Amorphous TiO₂ has been shown to exhibit low photoactivity (9), possibly due to decreased charge carrier mobility more easily attainable in definite crystal structures (10). Brookite is of no commercial significance and not used in photocatalysis. Of the remaining two forms, anatase has demonstrated the most photoactivity towards the degradation of organic compounds (3). Fox et al. (11) proposed that the lower photoactivity of rutile TiO₂ was due to its higher electron-hole recombination rate and its lowered capacity to adsorb oxygen, though Sclafani (11) found the activity of rutile to be influenced by its preparation conditions. Despite recent findings indicating that rutile TiO₂ may exhibit greater photoactivity towards certain compounds, particularly for the oxidation of CN⁻ (8), anatase is still the more practical form for widespread environmental applications. Anatase is thermodynamically less stable than rutile, though it is kinetically favored at temperatures < 600 °C (3). Optimizing the performance of titania with regards to annealing temperature has been the subject of several recent papers (8). Aside from the crystal

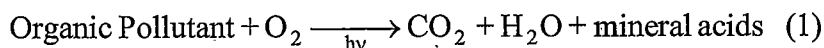
structure, the annealing conditions can control the morphology, specific surface area and surface density of OH groups (7). Hoffmann et al. (8) found the rates of 4-chlorophenol degradation to increase as the anatase form was calcined progressively from 100 to 400 °C and to decrease with TiO₂ calcined at 500 °C and above. Tanaka et al. (6) reported the degradation of several compounds to be dependent upon annealing conditions while independent for others. They also reported that TCE degradation rates increased for annealing temperatures up to 500 °C, and in some cases up to 700 °C, but decreased above those temperatures. Tsai et al. (11) found the photoactivity of laboratory produced rutile TiO₂ to decrease with calcination temperature and correlated it to the amount of OH groups on the surface. The general consensus seems to indicate that the photoactivity of titania decreases as the annealing temperature approaches the temperature of the rutile phase change (~600 °C). Moreover the higher annealing temperatures relieve the TiO₂ surface of OH groups essential to photoactivity. The increased photoactivity of anatase therefore is thought to arise from a larger surface area and a higher surface density of active sites for adsorption and photocatalysis.

The majority of titania used in photocatalysis comes in three forms: a pre-made TiO₂ powder, TiO₂ particles precipitated from a sol-gel, and TiO₂ produced by chemical vapor deposition (CVD) of titanium chlorides (TiCl₃ and TiCl₄) on some support. The pre-made powders come in a controlled crystal structure and particle size (generally anatase on the nm to μm scale). Starting from a titanium salt, sol-gel techniques can produce titania from a sequential process of hydrolysis, polycondensation and drying of a colloidal suspension (12). Sol-gels can generally produce small (~10nm) amorphous and

crystalline TiO₂ particles, where crystal structure and particle size is a function of preparation conditions (pre-cursor sol, calcining conditions, pH, etc.). Titania from CVD is obtained by exposing a surface to titanium chlorides and water vapor at high temperatures (~200–500 °C), where the water vapor will substitute for the chlorides. Ultrafine thin films of titania on silicon and quartz substrates have been reported using CVD techniques (13). Obviously, there are numerous variations on sol-gel and CVD techniques that can affect particle growth and crystal structure. The chemistry involved is beyond the scope of this paper. A good treatment of colloidal semiconductors can be found in Reference 3.

Mechanism for heterogeneous photocatalysis using TiO₂

Certain features of photoinduced reactions involving semiconductor catalysts have previously been mentioned. Some will be repeated here for clarity in the specific case of heterogeneous photocatalysis involving TiO₂ and the degradation of aqueous organic contaminants. The overall process of the photodegradation of organics with TiO₂ can be summarized as follows

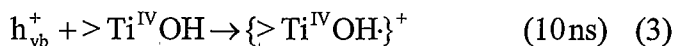


Though the exact mechanism for the heterogeneous photodegradation of aqueous organics is not completely understood, it is known that the primary process involves electron-hole pair formation followed by interfacial electron transfer to form surface bound oxidants (7). Based on laser flash photolysis measurements, Hoffman et al. (8) proposed the following mechanisms, with their characteristic times, for surface reactions on illuminated TiO₂.

Charge carrier generation



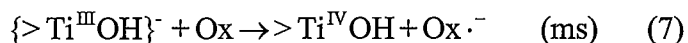
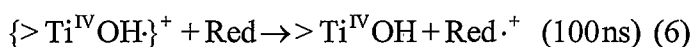
Charge carrier trapping



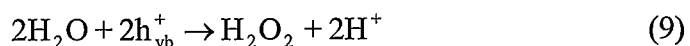
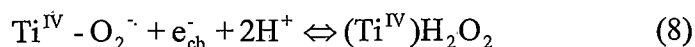
Charge carrier recombination



Interfacial charge transfer



The overall success of a photocatalytic reaction is dependent on the competition between charge carrier trapping and recombination (Equations 3-4 & 5). The above mechanism assumes all oxidation of organics occurs via surface bound hydroxyl $\{> \text{Ti}^{\text{IV}}\text{OH}\}^+$ attack, though oxidation may occur with between free radicals and liquid phase organics as well (14). Also not mentioned in this scheme is the formation of hydrogen peroxide from dioxygen reduction with conduction band electrons and possibly from valance band hole oxidation of water (15). These two pathways can be represented as follows (14, 15):



It has been noted that H_2O_2 may contribute to the degradation of pollutants by acting as a direct electron acceptor or as a further source of hydroxyl radicals due to homolytic splitting (15).

Though it is assumed that hydroxyl radicals are the primary oxidant in TiO_2 systems, it is not known if oxidation principally occurs via surface bound or free radicals.

Turchi and Ollis (14), in an effort to determine the role of hydroxyl radicals in TiO₂ photocatalysis, proposed four possible mechanisms for hydroxyl radical attack.

1. Reaction occurring while both organic and hydroxyl are adsorbed.
2. A non-bound radical reacts with a bound organic.
3. An adsorbed radical reacts with a free organic.
4. Reaction occurs between free radical and organic.

Four kinetic models were derived for the above, relating degradation of a single component by way of hydroxyl attack. All resembled Langmuir-Hinshelwood (L-H) rate forms.

$$r_i = \frac{k_{\text{obs}} \kappa C_i}{1 + \kappa C_i} \quad (10)$$

It was found that k_{obs} was the same for each of the four cases in the degradation of 14 organic compounds, suggesting that it is a function only of catalyst properties and reaction conditions. Further differentiating between reactions of adsorbed and free radical to suggest a dominant form was not possible. Estimates of diffusion/reaction rates with free OH radicals and liquid phase organics suggest that even at low organic concentration, free radicals would not diffuse very far into solution before reacting ($\sim 10^{-8}$ – 10^{-6} m). Based on these estimates, they found it plausible that OH is present as a mobile radical. It is likely that some combination of these mechanisms is present during heterogeneous photocatalysis.

In most photocatalytic systems, oxygen acts as an electron acceptor. The current view is that electrons are consumed by dioxygen to produce the superoxide radical anion,

O_2^- (1), with subsequent electron transfer reactions leading to the formation of H_2O_2 . Supporting this view is work by Serpone et al. that noted no degradation occurs in the absence of oxygen (3). Control batch experiments by our group in which aqueous phenol suspensions of TiO_2 were sparged with nitrogen also found no degradation to take place. Serpone has observed superoxide radicals on the surface of illuminated TiO_2 in the presence of oxygen (1). Hoffmann et al. (15), using ^{18}O isotopic labeling with a ZnO photocatalyst noted that all of the photochemically produced H_2O_2 is from dioxygen. They also reported that hydrogen peroxide was not detected in the absence of oxygen.

Catalyst Supports

Much of the work in liquid phase photocatalysis using TiO_2 has been conducted in slurry type reactors using very fine titania particles (e.g. Degussa P25 TiO_2 : ~30nm in diameter). These types of reactors have several advantages. In perfectly mixed reactors, there will be no segregation of phases and with fine particles (nm scale), the entire external surface can be illuminated during the reaction (12). Also these reactors have a large ratio of surface area of TiO_2 per unit volume of the reactor, limiting mass transfer effects (16). In modeling these systems, they can be (at least to a first approximation) treated as "pseudo-homogenous" and amenable to simple laws such as the Beer-Lambert law (12). Overall though, the utility of these reactors is limited, as recovery of the catalyst downstream of the reactor is difficult.

Fixing the catalyst on a support of some sort is the alternative. Certain tradeoffs come with immobilizing the catalyst though. Degradation rates may be mass transfer

limited and the catalyst-photon interactions will be more limited. These limitations will be dependent on specific reactor/support configurations.

Pozzo et al. (13), in a recent review of research on supported TiO_2 for use in environmental photocatalysis, suggested the following attributes of a good photocatalyst support:

1. Transparent to UV radiation.
2. Favor strong surface chemical-physical bonding with the TiO_2 particles without negatively affecting their reactivity.
3. Offer a high specific surface area.
4. Have good adsorption capability for the organic compounds to be degraded.
5. Be in a physical configuration which favors the ultimate liquid-solid phase separation.
6. Allow reactor designs that facilitate the mass transfer processes.
7. Be chemically inert.

Early work on immobilized photocatalysts involved coating the inner glass walls in an annular type reactor (17) or the inner wall of a glass coil wrapped around a circular light source (18, 19). Degradation rates for these flow-by type reactors were found to suffer from boundary layer mass transfer limitations, as only a portion of substrate will be in contact with the catalyst at any given time (20).

In the last decade, much attention has been directed towards immobilizing TiO_2 on various substrates including; particles (silica, alumina, zeolites, activated carbon, glass

beads etc.), quartz optical fibers, glass fiber or wool (12, 13). Various forms of reactor design have been employed, including packed, fluidized and floating bed reactors. Based on the current interest here, the following discussion will be restricted to particle supports applicable for packed bed applications.

Recent research has shown that supports can alter photoactivity in several ways. For example, Xu and Langford (21) comparing two different zeolites, silica gel, and alumina, related increased adsorption of organics on the support to increased photoactivity. Concerning zeolites, they proposed increased photoactivities could be related to the rigid framework of the surface, where reactive radicals, such as $\cdot\text{OH}$ and O_2^- , could be stabilized on the surface where they can be efficiently reached by organic molecules. Xu et al. (9), in a comparative study of preparation methods for coating silica gel with sol based TiO_2 , also related increased photoactivity to increased adsorption of organics. Rates reported for supported catalysts were considerably higher than those obtained with bare catalysts. In these experiments degradation rates were found to be higher with smaller silica gel particles. They reported that smaller silica particles resulted in the formation of smaller TiO_2 particles on the surface. It was suggested that smaller silica particles cause the TiO_2 to be more dispersed on the surface (possibly affecting crystallinity) and more efficient as a photocatalyst.

Surface characterization of supported catalysts is important in that the crystal structure of titania on the support can be determined and related to its photocatalytic behavior. Also, determining how TiO_2 is adhering to the support will allow predictions of the durability of a specific catalyst under reaction conditions. Xu et al. (9) found that

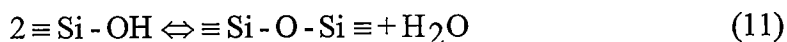
supporting TiO_2 on silica restricts crystal formation even after calcining. They reported a film of amorphous TiO_2 to exist on the surface, limiting photoactivity. Xu and Langford (21) found that at low coverage, TiO_2 on zeolite is amorphous, only forming well-defined anatase crystals at higher coverage. Structure determination of supported titania is made difficult at lower loadings commonly encountered in environmental photocatalysis (generally less than 1 wt. %). Differentiating between X-rays of the catalyst/support surface in X-ray diffraction (XRD) analysis is difficult at such low loadings, making the results suspect. Similarly, scanning electron microscopy (SEM) of supported surfaces reveals little about the true nature of the catalyst-support interactions. Islands of what appears to be titania have been reported to appear on supported surfaces (12), suggesting a random, highly dispersed coating. Xu and Langford (21) suggest that these particles may form on a thin coat of titania after monolayer capacity has been exceeded. Verifying this would require slicing a coated particle and viewing it from the side. This would allow determination of the thickness of a titania layer if it formed as a uniform coat. The small size of most support materials (μm – mm scale) makes this difficult and slicing would likely damage the coating.

TiO_2 adherence to the support is an essential aspect in supported photocatalysts, yet many papers on the subject neglect it entirely (9, 16, 18, 21). If supports readily lose their titania (or a substantial portion of it) to the fluid phase, the reason for its use is compromised. Adherence is generally evaluated at reaction conditions. Analysis of the catalyst after subjecting it to flows high enough to eliminate mass transfer concerns will allow quantification of adherence. Bideau et al. (12) in a comparison of supports, titania,

and coating methods, found pre-made powder (P25 TiO₂) coatings to adhere better to silica gel than coatings using a sol-gel process (loss of 52% for sol compared to 21% for P25 powder). Zhang et al. (22), using powder (Aldrich TiO₂) coated silica gels, reported no noticeable attrition of TiO₂ after 1 hour under flow and no decrease in photoactivity after a 20-day run. Though coating methods used by the Bideau and Zhang groups were similar for powder coatings, widely varying results were obtained. These results can be somewhat misleading in that reactor configurations differed. The setup used by Zhang et al. was a packed tubular reactor and that used by Bideau et al. was a CSTR with the catalyst placed on the bottom. It would be natural to assume that supported catalyst in a packed bed would be subjected to greater stress and yet they reported no loss of catalyst. Such results could be explained by the fact that different silica gels, titania powders, and calcining conditions will produce different coatings, one performing well and one not. This makes direct comparisons between different researchers difficult.

Silica Gel

In this study, silica gel (SiO₂) was chosen as a photocatalyst support for its ability to meet several of the above mentioned criteria. It transmits UV light well, has high specific surface area (~100-1000 m²/g) and is chemically inert. The surface of silica gel is covered by hydroxyl and siloxane groups. Hydroxyl groups can be arranged on the surface in various ways with one or two hydroxyls bound to a single Si atom (23). Siloxane groups are formed by a partially reversible dehydroxylation between hydroxyl groups at about 500 K (3). This can be represented as follows



In an aqueous environment, silica gel is capable of taking up water and organics by means of physical adsorption (23), with the amount dependent on temperature, surface density of hydroxyl groups, pH, and specific surface area. The point of zero charge (PZC) for most silica gels is at a pH of about 2 (3). Above this pH, the surface will be negatively charged, limiting its adsorptive capabilities for negatively charged ions. Aside from the above support criteria, silica gels also exhibit high thermal stability and high mechanical strength (24).

Coating a support with sols or pre-made powders generally involves mechanical mixing of a liquid suspension of titania and the support material followed by calcining and washing. For the case of silica gel, titania bonding likely occurs at surface hydroxyls with the attraction being Van der Waals forces (24). The degree of dispersion of titania on silica will therefore be dependent on the surface density of hydroxyls on silica (and also titania particle size) (24). This surface density of hydroxyls will change with calcining temperature. With other coating methods such as CVD there is evidence of Ti-O-Si linkages at the surface, which will alter the electronic properties of the catalyst (24).

Photoreactors

Photodegradation rates will be dependent on reactor design, as the geometry will determine light distribution. Numerous reactor designs utilizing sunlight and artificial light have been employed in photocatalytic work and are described elsewhere (4, 8, 17, 22, 25, 26). By far, the configuration most used in bench scale operations is the lamp in tube annular reactor. This reactor represents a simple and very efficient configuration utilizing artificial light (27) and is probably the best type for commercial applications.

