Aluminum oxide for photocatalytic organic transformations

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**ALUMINUM OXIDE FOR PHOTOCATALYTIC
ORGANIC TRANSFORMATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

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**SCHOOL OF MATERIALS SCIENCE AND
ENGINEERING**

A thesis submitted to the Nanyang Technological University
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Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

28 Jul 2016

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Date

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Abstract

The use of sunlight to drive organic reactions constitutes a green and sustainable strategy for organic synthesis. In such reactions, the photoredox requirements of organic reactions are typically fulfilled through using wide band gap semiconductors or redesigning the photocatalyst. Herein, we demonstrated the use of a reverse strategy; instead of redesigning the dye as per convention, the reactant is chemisorbed on the Brønsted base sites of Al_2O_3 to form a surface complex, causing an upshift in its HOMO to a level accessible for electron abstraction by the dye. This enables the highly selective oxidation of benzylic alcohols to aldehydes by a large variety of dyes, even though negligible reaction occurred in the absence of Al_2O_3 or with other metal oxides. The charge-transfer surface complex formed between the dye and Al_2O_3 is also essential in facilitating the transport of electrons from BnOH to O_2 .

Next, we further extended the use of Al_2O_3 complexation in conjunction with photocatalysis to drive the selective aerobic oxidation of phenylboronic acids. It was discovered that all metal oxides with Brønsted basicity can also enable high yields of phenols. The proximity and strength of the Brønsted base sites appear to be crucial towards the reaction; there seems to be a positive relationship between the yields of alcohol and the quantity of strong Brønsted base sites, rather than with the quantity of weak or all Brønsted base sites.

Lastly, we explored the idea of rendering Al_2O_3 photocatalytically active through carbon-modification, which would eliminate the need for a dye. The resultant carbon doped Al_2O_3 enables the selective oxidation of benzylic amines to form imines under visible light irradiation. We believe that our aforementioned discoveries may subvert our understanding of the role of Al_2O_3 in photocatalytic reactions. It may also bring forth a new methodology of utilizing surface complexation mechanisms between the reactants and earth-abundant materials to effectively achieve a wider range of photoredox reactions.

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Abbreviations

ACA	9-Anthracenecarboxylic acid
Al ₂ O ₃	Aluminum Oxide
BnOH	Benzylalcohol
BET	Brunauer–Emmett–Teller
FTIR	Fourier Transform Infrared Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
NTCDA	1,4,5,8-Naphthalenetetracarboxylic dianhydride
PTCDA	perylene-3,4,9,10-tetracarboxylic dianhydride
PXRD	Powder X-ray Diffraction
Ru(bpy) ₃ ²⁺	Ruthenium(II) tris(2,2-bipyridine)
SAED	Selected Area Electron Diffraction
TMPP	5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

In this chapter, the hypotheses, objective, overview and outcomes of this dissertation will be presented. Under the section 'Hypotheses/Problem statement', the key motivation behind this research, which to reduce the detrimental environmental impact of chemical industries through the alternative strategy of photoredox catalysis, will be addressed. To further develop the field of photoredox catalysis, aluminum oxide catalysis is believed to play a potential role in enabling even more possible organic transformations. To achieve this, the hypotheses to be tested will be first identified. Next, in the objective section, the goal of this dissertation will be disclosed, which is to utilize the surface properties of Al_2O_3 to extend the range of photocatalytic organic reactions available. Next, an outline of the individual chapters covered in this dissertation will be provided under the section 'Dissertation Overview'. Lastly, the outcomes achieved in this thesis will be summarized in the section 'Findings and outcome/Originality'.

1.1 Hypothesis/Problem Statement

Photoredox catalysis is an increasingly popular method for difficult organic transformations, as it shows great promise for the production of industrially-valuable products under mild conditions and with less toxic reagents ^{1,2}. For example, the selective oxidation of aromatic alcohols to aldehydes, an important method for converting raw materials into fine chemicals³⁻⁵ especially in the flavor and fragrance industry ^{6,7}, typically requires stoichiometric amounts of toxic oxidants, which have deleterious effects on both human health and the environment ⁸⁻¹¹. Not only that, visible light is also an environmentally-friendly and cost-effective energy source.

In the past development of photocatalysis, alumina has played a supporting rather than a central role. This is because alumina is paradigmatically known as an electrical insulator, and has been extensively used as such, i.e., as protective wire casings, gate insulators ¹², and photochemically inert barriers to prevent undesired electron pathways during photocatalytic reactions ^{13,14}. However, alumina, in particular the γ -crystalline phase, possesses unique surface characteristics, such as bifunctional Brønsted acid and base sites ¹⁵, abundant Lewis acid and base sites ¹⁶, and the ability to sustain high surface areas ¹⁷. These characteristics have led to the widespread use of Al_2O_3 as a catalytic support to endow supported materials with catalytic activity that is absent in the pristine materials alone ^{18,19}. In this dissertation, we propose that the unique surface properties of Al_2O_3 can be utilized in conjunction with photosensitizers to enable difficult organic transformations. This will be elaborated by the following hypotheses.

1.1.1 First Hypothesis: The Redox Potential of the Reactant may be reduced through Complexation with Alumina to Enable Photocatalytic Organic Transformations

In the aforementioned photocatalytic redox reactions, reaction can proceed only if the redox potential of the photocatalyst is greater than that of the organic reactants²⁰. Conventional strategies to fulfill this condition have involved the use of wide band gap semiconductors²¹ such as TiO_2 ^{3,6,22-28} or Nb_2O_5 ^{29,30}, as well as the redesign of a photocatalyst by changing the cation^{20,31-33} or the ligands of transition metal complexes to tune the reduction potential^{20,34}. However, the former method is unable to access the longer wavelength range of the solar spectrum, while the latter requires unique photocatalysts to be synthesized for specific reactions. Based on the aforementioned merging of photocatalysis with other types of catalysis for different purposes, we hypothesize that the redox potential of the reactant may be reduced through complexation with another catalyst such as alumina, which would render it susceptible to oxidation or reduction by photocatalysts with smaller redox potentials.

1.1.2 Second Hypothesis: The Brønsted and Lewis Acid and Base Sites on the Surface of Al_2O_3 can participate as a Co-Catalyst in Photocatalytic Organic Transformations

The surface of Al_2O_3 is also decorated with bifunctional Brønsted and Lewis acid and base sites,¹⁵ which enable it to support certain catalytic reactions through the abstraction and release of protons.³⁵ We hypothesize that these bifunctional Brønsted acid and base sites can also be used to support photocatalysts to enable a wider range of photocatalytic organic transformations.

1.1.3 Third Hypothesis: The Surface Properties of Al_2O_3 and the Photosensitizer can be combined as a Single Catalyst through Extrinsic Doping

Due to the large band gap of Al_2O_3 , no electrons in the valence band can jump to the conduction band under the solar light illumination. To this aim, extrinsic ion doping of insulators may represent a valuable way to obtain novel semiconductors from modified insulators. Our last hypothesis is that the dye- Al_2O_3 surface complex system can be simplified through the combination of photocatalysis and Al_2O_3 surface catalysis in a single material. This is achieved through the carbon doping of Al_2O_3 , in order to sensitize it to visible light irradiation.

1.2 Objectives and Scope

In this thesis, our objective is to utilize the surface properties of Al_2O_3 in order to extend the range of photocatalytic organic transformations achievable. To demonstrate this, we will undertake the following:

1. Investigation into the surface properties of Al_2O_3 .
2. Demonstration of the application of Al_2O_3 , which is paradigmatically known to be an insulator, in photoredox organic transformations.
3. Demonstrate the use of carbon-doping to render Al_2O_3 photocatalytically active under visible light irradiation.

1.3 Dissertation Overview

The thesis seeks to provide an overview on the unique surface properties of Al_2O_3 and how these can be utilized for photoredox reactions. A total of 8 chapters will be presented in the following sequence:

Chapter 1 introduces the motivation for research into photoredox reactions and the rationale for aluminum oxide as the catalyst of choice. The objectives and scope are also outlined in this chapter.

Chapter 2 reviews the literature concerning the current progress in the types of photoredox reactions achievable as well as the catalysts used.

Chapter 3 discusses the principles underlying the synthesis/characterization/modeling techniques employed and the methods of data analysis, including errors.

Chapter 4 demonstrates the use of Al_2O_3 and dye surface complex system for the photocatalytic organic transformation of phenylboronic acids to phenols.

Chapter 5 demonstrates the use of Al_2O_3 and dye surface complex system for the photocatalytic organic transformation of benzylalcohols to benzaldehydes.

Chapter 6 demonstrates the use of carbon-doping as a means to render the insulator Al_2O_3 photocatalytically active under visible light irradiation.

Chapter 7 discusses the extent to which the hypotheses were proven, and elaborates on how the design target is met.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes.

1. The strong Brønsted and Lewis base sites on the surface of Al_2O_3 has been used to enable the photocatalytic selective oxidation of phenylboronic acids to phenols.
2. The redox potential of reactants can be reduced through surface complexation with Al_2O_3 . This is utilized for the selective photocatalytic oxidation of benzylalcohols to benzaldehydes.
3. The surface complexation of O_2 with Al_2O_3 also activates the adsorbed O_2 for receiving electrons from the photoexcited dyes.
4. Carbon doping can be used to sensitize Al_2O_3 to visible light irradiation. This is utilized for the selective photocatalytic oxidation of benzylamines to imines with high conversions and selectivities.

Chapter 2

Literature Review

In this chapter, the advances in photoredox catalysis will be discussed, namely with regards to two types of photocatalysts; metal oxide semiconductors and ruthenium(II) tris(2,2-bipyridine) complex. Next the recent emerging concept of dual photoredox catalysis will be discussed, in which photocatalysis is paired with other types of catalysis to achieve a wider range of reactions possible. The properties of aluminum oxide and the possible applications of this material to catalysis will be then be discussed. Lastly, the questions arising from literature review will be addressed; whether aluminum oxide catalysis can be coupled with photocatalysis to increase the scope of organic transformations possible.

2.1 Photoredox Catalysis

Recently, there has been increasing interest in the development of green synthesis processes based on renewable energy, in order to diminish the negative impact on the environment associated with the chemical industry. Sunlight, being an abundant and clean energy resource, possesses great potential as the driving force for environmentally friendly organic transformations.¹ The generation of free radicals through the absorption of solar energy constitutes an alternative route for difficult organic transformations, thus enabling such reactions to occur under ‘milder’ conditions and with minimal toxic reagents^{1,2}. To this end, a plethora of selective photocatalytic organic transformations and photocatalysts were developed. In this section, we will discuss the different photocatalytic organic transformations that are achievable with two popular categories of photocatalysts; metal oxide semiconductors and ruthenium(II) tris(bipyridine) complex. We will also discuss dual photocatalysis, an emerging concept that combines the typical photocatalysis with other types of catalysis in order to achieve an extended range of organic transformations.

2.1.1 Metal Oxide Semiconductors

Large band gap metal oxide semiconductors such as TiO_2 , Nb_2O_5 and ZnO are favoured as catalysts for photocatalytic organic transformations as the LUMO and HOMO of most organic reactants would be within the conduction (CB) and valence bands (VB), thus rendering the reactant susceptible to reduction and oxidation, respectively.³⁶ Hence, these wide band gap semiconductors are typically the catalysts of choice for the photodegradation of organic pollutants in water. However, the large band gap of these semiconductors requires UV light in order to undergo photexcitation.^{37,38} Most organic molecules of interest also absorb light only in the low wavelength UV region. For solar energy to be harvested effectively, the full spectrum of sunlight including the visible range must participate in driving the organic reactions. Not only that, visible light, being less robust than UV light, can improve the selectivity of organic

transformations.³⁶ In recent years, it has been discovered that the surface complexes formed between certain organic reactants and the surface of these metal oxide semiconductors can absorb visible light to generate electron-hole pairs, thus facilitating the organic transformations. The following will describe some notable examples of selective organic transformations that have been achieved through such surface complexation with metal oxide semiconductors.

Organic compounds containing heteroatoms such as O, N or S can easily adsorb to the surface of metal oxide semiconductors, creating a donor level corresponding to the 2p orbital of the heteroatoms. When exposed to visible light irradiation, electrons can be promoted from the donor levels to the CB of the metal oxide semiconductors, thus facilitating the selective transformations of the organic compounds. An example is the selective photocatalytic oxidation of benzylalcohols to benzaldehydes by oxygen on a TiO₂ photocatalyst under visible light irradiation (**Figure 2.1**).⁶ The antibonding π molecular orbitals of benzylalcohol can hybridize with the O 2p atomic orbitals of TiO₂, allowing the electrons in the occupied orbitals of benzylalcohol to be promoted to the TiO₂ conduction band along with the electrons in the TiO₂ valence band (**Figure 2.2**).³⁹ Oxygen isotope studies through the use of ¹⁸O-enriched benzylalcohol and TiO₂ with ¹⁸O-enriched surface OH groups yielded 100% ¹⁶O abundance in the product.⁴⁰ From this, it was proposed that the benzylalcohol is furnished with molecular oxygen from the atmosphere (**Figure 2.3**). The benzylalcohol molecule accepts the photogenerated hole to form a carbon radical while Ti_{IV} accepts the electron to form Ti_{III} (II). This renders the surface complex susceptible to attack by molecular oxygen, and the subsequent cleavages of the C-O bond of benzylalcohol and the O-O bond of oxygen results in the formation of the product benzaldehyde.⁴⁰ Besides TiO₂, Nb₂O₅ can also serve as a catalyst for the selective photocatalytic oxidation of benzylalcohols by oxygen (**Figure 2.4**).³⁰

Figure 2.1 Selective aerobic oxidation of benzylalcohol to benzaldehyde with TiO₂ under visible light irradiation.⁶

Figure 2.2 Schematic illustration of band gap modification in TiO₂ by adsorbed benzylalcohol molecules.³⁹ Reproduced with permission from reference 39. Copyright 2011, American Chemical Society.

Figure 2.3 Proposed oxygen transfer process in photocatalytic oxidation of benzylalcohol on TiO₂ in the presence O₂.⁴⁰ Reproduced with permission from reference 40. Copyright 2011, Wiley.

Figure 2.4 Selective aerobic oxidation of benzylalcohol to benzaldehyde with TiO_2 under visible light irradiation.³⁰

Another photocatalytic transformation involving a heteroatom-containing compound is the selective aerobic oxidation of benzylamines to imines by TiO_2 or Nb_2O_5 under visible light (**Figure 2.5**).^{29,41} The photogenerated hole is received by benzylamine while the electron is transferred to the metal oxide semiconductor, after which benzylamine is simultaneously furnished by molecular oxygen and subjected to C-N bond cleavage to form benzaldehyde. The resultant benzaldehyde then reacts with the remaining benzylamine to form imine (**Figure 2.6**).^{41,42}

Figure 2.5 Selective aerobic oxidation of benzylamine to imine with TiO_2 and Nb_2O_5 under visible light irradiation.^{35,43}

Figure 2.6 Proposed oxygen transfer process in photocatalytic oxidation of benzylamine on TiO_2 in the presence O_2 .⁴⁰ Reproduced with permission from reference 40. Copyright 2011, Wiley.

Besides O₂, other nucleophiles can also be used for incorporation into heteroatom organic compounds. For instance, -CH₂NO₂ and -CN have successfully been incorporated into N-aryl-tetrahydroisoquinolines through TiO₂ catalysis, resulting in the formation of C-C bonds (**Figure 2.7a** and **b**, respectively).⁴³ Such reactions are extremely robust; high yields could be obtained under illumination by a standard household 11 W fluorescent lamp.

Figure 2.7 Visible light induced C-C bond formation on the surface of TiO₂.⁴³ Nucleophilic attack by (a) nitromethane, and (b) cyanide.

2.1.2 Ruthenium(II) tris(2,2-bipyridine) complex

In order to use sunlight to enable reactions, the photocatalyst must effectively absorb sunlight to achieve electron-hole separation. Nature, which utilizes various visible-light-absorbing chromophores during photosynthesis, has inspired much research on different photo-absorbing molecules and complexes to convert solar energy to chemical energy.²⁰ Out of these, ruthenium(II) polypyridine complexes, in particular ruthenium(II) tris(2,2-bipyridine) (Ru(bpy)₃Cl₂), have attracted immense popularity due to their ease of synthesis, stability, and good photoredox capabilities. Hence, this chapter will focus on the types of photocatalytic organic transformations that can be achieved with Ru(bpy)₃Cl₂.

$\text{Ru}(\text{bpy})_3\text{Cl}_2$ is a transitional metal complex that absorbs visible light with λ_{max} at 452 nm, which leads to a metal-to-ligand-charge-transfer (MLCT) and generates the excited state $\text{Ru}(\text{bpy})_3^{2+*}$. $\text{Ru}(\text{bpy})_3^{2+*}$ can be oxidatively quenched to form the strong oxidizing agent $\text{Ru}(\text{bpy})_3^{3+}$ (1.29 V vs. SCE), or reductively quenched to form the strong reducing agent $\text{Ru}(\text{bpy})_3^+$ (1.33 V vs. SCE) (**Figure 2.8**).²⁰ The generated $\text{Ru}(\text{bpy})_3^{3+}$ or $\text{Ru}(\text{bpy})_3^+$ then accepts or donates an electron in a process commonly known as the single electron transfer (SET) process to achieve the oxidation or reduction of the reactant, respectively. Such versatile photoredox capabilities makes $\text{Ru}(\text{bpy})_3^{2+}$ the most widely used photocatalyst for organic synthesis.

Figure 2.8 Scheme of photoredox processes for $\text{Ru}(\text{bpy})_3\text{Cl}_2$.²⁰ Reproduced with permission from reference 21. Copyright 2011, the Royal Society of Chemistry.

2.1.2.1 Oxidation Reactions

The following are some examples of photoredox reactions achieved through the oxidative quenching pathway of $\text{Ru}(\text{bpy})_3^{2+}$:

1. Synthesis of phenathrene from stilbenediazonium salt via Pschorr reaction (**Figure 2.9**).⁴⁴ The absorption of light by $\text{Ru}(\text{bpy})_3^{2+}$ generates the excited state $\text{Ru}(\text{bpy})_3^{2+*}$, which donates an electron to the stilbenediazonium cation to form $\text{Ru}(\text{bpy})_3^{3+}$ and an aryl radical. The aryl radical undergoes internal arylation and subsequent oxidation by $\text{Ru}(\text{bpy})_3^{3+}$ to form phenathrene.

Figure 2.9 Pschorr reaction achieved through photocatalysis with $\text{Ru}(\text{bpy})_3\text{Cl}_2$.⁴⁴

2. Selective oxidation of benzylalcohols by a RuL_3^{2+} complex (**Figure 2.10**).³⁴ Similar to the previous reaction, aryl diazonium cation was used to quench the excited state RuL_3^{2+*} to form RuL_3^{3+} and an aryl radical. The oxidant RuL_3^{3+} then removes an electron from benzylalcohol, after which it loses protons to the aryl radical and an organic base collidine to form benzaldehyde.

Figure 2.10 Selective oxidation of benzylalcohols with RuL_3^{2+} photocatalyst and aryl diazonium cation as the oxidative quencher.³⁴

3. Selective oxidation of sulfides, another benzylic heteroatom reactant like benzylalcohol, to sulfoxides (**Figure 2.11**).⁴⁵ Instead of an aryldiazonium cation, O_2 was used to oxidatively quench the excited state $Ru(bpy)_3^{2+*}$ to form $Ru(bpy)_3^{3+}$. $Ru(bpy)_3^{3+}$ then oxidizes the sulfide to form sulfoxide. This reaction is considered environmentally benign as it uses the clean and abundant resource O_2 as the sacrificial agent.

Figure 2.11 Photocatalytic aerobic oxidation of sulfides to sulfoxides by $Ru(bpy)_3Cl_2$.⁴⁵

2.1.2.2 Reduction Reactions

Besides oxidative organic transformations, $Ru(bpy)_3^{2+}$ can also be used to achieve reduction reactions with the use of a reductive quencher.⁴⁶ The following are some examples of photoredox reactions achieved through the reductive quenching pathway of $Ru(bpy)_3^{2+}$:

1. Photocatalytic reduction of phenacylhalides (**Figure 2.12**).⁴⁷ Dihydroacridines is used to reductively quench $Ru(bpy)_3^{2+*}$ to produce $Ru(bpy)_3^{+}$. Interestingly, when high concentrations of acid is added into the system, the phenacylbromide becomes the oxidative quencher to produce $Ru(bpy)_3^{3+}$ for the oxidation of dihydroacridine. This mean that though the same products are obtained, the pH of the system controls whether the reaction follows an oxidative or reductive pathway, which shows the versatility of $Ru(bpy)_3^{2+}$.

Figure 2.12 Photocatalytic reductive dehalogenation of phenacylhalides by $\text{Ru(bpy)}_3\text{Cl}_2$.⁴⁷

2. Decarboxylation of acyloxyphthalimides for subsequent addition,⁴⁸ reduction⁴⁵ or phenylselenation^{49,50} (**Figure 2.13**). BNAH (1-benzyl-1,4-dihydronicotinamide) is used as the reductive quencher to produce Ru(bpy)_3^+ , which removes a single electron from the acyloxyphthalimide to generate alkyl radicals. The radicals can then be captured by different electrophiles to form C-C, C-H or C-Se bonds.

Figure 2.13 Photoredox decarboxylation of acyloxyphthalimides and subsequent addition, reduction or phenylselenation by $\text{Ru(bpy)}_3\text{Cl}_2$.⁴⁸⁻⁵¹

3. Photocatalytic reductive opening of the C_α-O bond of ketoepoxides to form β-hydroxy ketones (**Figure 2.14**).⁵² This is achieved by using N,N-dimethylbenzimidazoles as the proton donor and reductive quencher to produce Ru(bpy)₃⁺. Single electron donation by Ru(bpy)₃⁺ and subsequent proton abstraction causes the epoxide to open and selectively yield β-hydroxy ketones.

Figure 2.14 Photoredox reductive opening of ketoepoxides by Ru(bpy)₃Cl₂.⁵²

4. Selective [2+2] cycloaddition of aryl enone to form cis-cyclobutanes with ⁱPr₂Net as the reductive quencher to obtain Ru(bpy)₃⁺ (**Figure 2.15a**).⁵³ It is proposed that Ru(bpy)₃⁺ then reduces an aryl enone coordinated to a lithium ion. The aryl enone radical then undergoes 1,4-addition and radical cyclization with another aryl enone, resulting in the formation of the cis-cyclobutane product. An organic compound with two aryl enone groups can also undergo intramolecular [2+2] cycloaddition to form cis-cyclobutanes (**Figure 2.15b**).⁵⁴

Figure 2.15 Photocatalytic **a)** intermolecular and **b)** intramolecular [2+2] cycloaddition of aryl enones to cis-cyclobutanes by Ru(bpy)₃Cl₂.^{53,54}

2.1.3 Dual Photoredox Catalysis

Recent years have witnessed rapid advances in the types of organic transformations achievable due to dual photoredox catalysis, in which photocatalysis is merged with other forms of catalysis, such as organocatalysis and nickel catalysis. This offers certain advantages that are not present in each type of catalysis individually. For example, organocatalysis has been well-established for enantioselective C-C, C-O, C-N, and C-X (where X refers to a halogen atom),⁵⁵⁻⁵⁸ but it requires a two electron transfer from an electron-rich reactant to an electron-poor reactant. Photocatalysis, on the other hand, is capable of single electron transfer (SET). By combining the two types of catalysis, singly occupied molecular orbital (SOMO) organocatalysis would be enabled.^{46,59-62} SOMO catalysis generally involves the binding of an aldehyde reactant to a secondary amine catalyst to form enamine, which undergoes SET to an oxidant to form an enamine radical. The α -carbon of electron-deficient radical is susceptible to attack by a nucleophile. After oxidation and hydrolysis, the secondary amine catalyst would then release the product. The following are some examples of SOMO catalysis:

1. Photocatalytic enantioselective alkylation of aldehydes (**Figure 2.16**).⁶³ In this reaction, $\text{Ru}(\text{bpy})_3^{2+*}$ is the oxidant that receives an electron from the enamine to form $\text{Ru}(\text{bpy})_3^+$ and an enamine radical. The nucleophile is a alkyl radical generated from the C-X cleavage of phenacylhalide by $\text{Ru}(\text{bpy})_3^+$. This leads to the formation of an enantiomeric C-C bond.

Figure 2.16 Enantiomeric α -alkylation of aldehydes by SOMO catalysis.⁶³

2. Photocatalytic enantioselective trifluoromethylation of aldehydes (**Figure 2.17**).³¹ $\text{Ir(ppy)}_2(\text{dtbbpy})^{+*}$ is the oxidant that receives an electron from the enamine to form $\text{Ir(ppy)}_2(\text{dtbbpy})^+$ and an enamine radical. The nucleophile is a trifluoromethyl radical generated from the C-I cleavage of CF_3I by $\text{Ir(ppy)}_2(\text{dtbbpy})^+$. This also leads to the formation of an enantiomeric C-C bond.

Figure 2.17 Enantiomeric α -trifluoromethylation of aldehydes by SOMO catalysis.³¹

3. Photocatalytic oxyamination of aldehydes (**Figure 2.18**).⁶⁴ Ru(bpy)_3^{2+*} is the oxidant and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) is the nucleophile that attacks the enamine radical to form a C-O bond.

Figure 2.18 Photocatalytic α -oxyamination of aldehydes.⁶⁴

4. Photocatalytic continuous reductive cleavage of picolinium esters (**Figure 2.19**).⁶⁵ The anime that reacts with the carbonyl group is 8-oxoguanidine connected to the photocatalyst Ru(bpy)_3^{2+} . The reactants occurs through the cleavage of C-O bond to produce a picolinium radical through the release of a decanoate anion. The picolinium radical is then protonated to form a carboxylic

acid group. A similar reaction is the photocatalytic continuous reductive cleavage of 2-cyanopicolinium esters, in which ascorbic acid is used as the electron donor instead of 8-oxoguanidine (**Figure 2.20**).⁶⁶

Figure 2.19 Photocatalytic continuous reductive cleavage of picolinium esters.⁶⁵

Figure 2.20 Photocatalytic continuous reductive cleavage of 2-cyanopicolinium esters.⁶⁶

- Photocatalytic functionalization of indoles and pyrroles through intramolecular radical cyclization (**Figure 2.21**).⁶⁷ Et₃N is used as an electron donor to generate Ru(bpy)₃⁺, which cleaves C-X bond⁶⁸⁻⁷⁰ on the indoles and pyrroles to form a radical. The electrophilic radical attacks the electron-rich aromatic ring of the indoles and pyrroles, resulting in an intramolecular cyclization.

Figure 2.21 Photocatalytic functionalization of indoles and pyrroles through intramolecular radical cyclization.⁶⁷

6. Photocatalytic aza-Henry reaction with N-aryltetrahydroisoquinolines.⁷¹ N-aryltetrahydroisoquinolines undergoes SET to $\text{Ir(ppy)}_2(\text{dtbbpy})^{+*}$ to form an iminium ion. This can be trapped by simple nucleophiles that also function as the solvent, such as CH_3OH to CH_3NO_2 (**Figure 2.22**).

Figure 2.22 Mechanism of the photocatalytic aza-Henry reaction with N-aryltetrahydroisoquinolines.⁷¹

2.2 Aluminum Oxide

Aluminum oxide (Al_2O_3) is a material that possesses applications in many industries due to its advantageous properties, such as abundance, low cost, and resistance to corrosion. Al_2O_3 exists in several transition crystalline phases, such as $\gamma\text{-Al}_2\text{O}_3$, $\delta\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, and $\alpha\text{-Al}_2\text{O}_3$ the most stable form.⁷² Among these, $\gamma\text{-Al}_2\text{O}_3$ is the most widely studied due to its unique surface properties, such as its low surface energy, which enable it sustain high surface areas.¹⁷ The surface of $\gamma\text{-Al}_2\text{O}_3$ is also decorated with bifunctional Brønsted acid and base sites¹⁵ and abundant Lewis acid and base sites,¹⁶ which are of interest due to potential applications as catalysts and catalyst supports.⁷³ The crystal structure of $\gamma\text{-Al}_2\text{O}_3$ remains widely debated, but is typically considered to be a defect cubic spinel comprising a cubic close-packed stacking of O layers with Al atoms in the octahedral and tetrahedral sites, as well as some Al vacancies at the octahedral

positions to maintain the Al_2O_3 stoichiometry (**Figure 2.23**).¹⁶ Thus, a more appropriate formula for $\gamma\text{-Al}_2\text{O}_3$ would be $\text{U}_{2(2/3)}\text{Al}_{21(1/3)}\text{O}_{32}$, in which U indicates a cation vacancy. In integer terms, for every 3 unit cells, there should be 160 atoms, 96 O atoms, 64 Al atoms and 8 vacancies.

Figure 2.23 Unit cell of the defect cubic spinel $\gamma\text{-Al}_2\text{O}_3$ structure.¹⁶ Reproduced with permission from reference 16. Copyright 2005, Wiley.

As a catalyst, Al_2O_3 is widely used in a variety of industrial reactions. Some of its common applications are the catalysis of the Claus process, in which hydrogen sulfide is removed from waste gases through conversion into elemental sulfur, and the dehydration of alcohols to alkenes. At the laboratory scale, Al_2O_3 has been demonstrated to drive several organic reactions at mild conditions, ranging across intra- and intermolecular additions and substitutions, oxidations and reductions, as well as eliminations.⁷⁴ Some examples include the intramolecular addition of a carbonyl group to an adjacent alkene bond (**Figure 2.24a**), and the selective reduction of α,β -unsaturated aldehydes to the corresponding allylic alcohols (**Figure 2.24b**). The proposed role of Al_2O_3 is to position the adsorbed substrates closely to each other in the proper orientation⁷⁵ and to reduce the activation energy of the substrates for reaction.⁷⁴

Figure 2.24 Examples of organic reactions catalyzed by Al_2O_3 .⁷⁴ **a)** Intramolecular addition of a carbonyl group to an adjacent alkene bond. **b)** Selective reduction of α,β -unsaturated aldehydes to the corresponding allylic alcohols.

Due to the aforementioned ability to sustain high surface areas,¹⁷ Al_2O_3 is widely used as a catalyst support for reactions such as industrial hydrodesulfurization and Ziegler-Natta polymerization. It has been reported that Al_2O_3 may be able to endow supported materials with unique functionalities that are absent in the pristine materials.^{18,19} For instance, the activation of O_2 at the interface between Au clusters and Al_2O_3 enhances CO oxidation (**Figure 2.25a**).⁷⁶ Ag clusters supported on Al_2O_3 enable effective alcohol dehydrogenation³⁵ and subsequent amide synthesis⁷⁷ compared to that on other metal oxides due to the Al_2O_3 bifunctional acid-base surface; the base sites abstract protons from alcohol, while the acid sites promote the release of H_2 (**Figure 2.25b and c**). V_2O_5 loaded on Al_2O_3 has been reported to show significantly higher

activity during photo-oxidation of cyclohexane compared to that loaded on SiO_2 , TiO_2 or ZrO_2 , as the strong affinity of Al_2O_3 for vanadium ions enables the formation of isolated photoactive VO_4 species and prevents their polymerization into photocatalytically inactive V_2O_5 species.⁷⁸ These examples demonstrate that the surface characteristics of Al_2O_3 may extend the types of reactions available for the supported catalyst.

Figure 2.25 Al_2O_3 endows supported materials with catalytic activity that is absent in the pristine materials.⁷⁶ **a)** Activation of O_2 at $\text{Au}/\text{Al}_2\text{O}_3$ interface. **b)** Alcohol dehydrogenation³⁵ and **c)** amide synthesis⁷⁷ on Al_2O_3 supported Ag clusters. **d)** Photo-oxidation of cyclohexane by V_2O_5 loaded on Al_2O_3 (VA), SiO_2 (VS), TiO_2 (VT) or ZrO_2 (VZ). Reproduced with permission from references 20, 76, 77. Copyright 2006, 2009 and 2011, Wiley and Royal Society of Chemistry.

2.3 Questions Arising Regarding the Use of Aluminum Oxide Catalysis in Conjunction with Photoredox Catalysis

Al_2O_3 is paradigmatically known as an electrical insulator with an extremely large band gap of 7.6 eV. Due to this, Al_2O_3 tends to play a supporting rather than a central role in photocatalysis. However, photoluminescence studies indicate that Al_2O_3 is able to accept electrons from photoexcited materials such as $\text{g-C}_3\text{N}_4$ ⁷⁹ (**Figure 2.26**) and $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ ⁸⁰ to enhance photocatalytic reactions such as hydrogen generation from water and dye degradation, which is attributed to the presence of surface states far below the conduction band.⁸¹ This suggests that Al_2O_3 may be able to re-direct the electron transfer pathways to enhance the efficacy of photocatalytic reactions. Not only that, given the aforementioned surface properties of Al_2O_3 such as the presence of strong Brønsted acid and base sites, we propose that the Al_2O_3 can be used as a catalyst to support photoredox catalysis and extend the range of organic transformations achievable. However, current understanding of such electron transfer mechanisms is not extremely clear, and more investigations will need to be conducted in order to elucidate the Al_2O_3 energy structure and its surface interactions with neighbouring materials or molecules.

Figure 2.26 Scheme of photoluminescence occurrence in **a)** pristine Al_2O_3 and $\text{g-C}_3\text{N}_4$ and **b)** the $\text{Al}_2\text{O}_3/\text{g-C}_3\text{N}_4$ interface.⁷⁹

Chapter 3

Experimental Methodology

In this chapter, the rationale behind our choice of materials and methods will be presented. An overview of the characterization and analysis techniques will be provided over the next few sections, in which the working principles of instrument used will be elaborated. The techniques discussed comprise the following:

- *Gas chromatography*
- *Powder X-ray diffraction*
- *Brunauer–Emmett–Teller surface area analysis*
- *Temperature programmed desorption analysis*
- *Time-resolved photoluminescence spectroscopy*
- *Cyclic voltammetry*

3.1 Rationale for Selection

3.1.1 Materials

Dyes are selected as the photosensitizer in this research as they are robust and possess a large variety of different electronic and chemical properties. Al_2O_3 is selected as the catalyst as it is cheap, abundant, and non-toxic. Not only that, Al_2O_3 possesses a plethora of ideal catalytic characteristics such as large surface area, large quantities of surface acid and base sites, and the ability to separate electron-hole pairs to delay recombination. SiO_2 and MgO are chosen as the metal oxide catalysts for comparison with Al_2O_3 as both are insulators that are stable at high surface areas.

3.1.2 Methods

For the photocatalytic organic transformations, the catalyst and the reactant were added to the solvent in a Pyrex vessel sealed with an aluminum crimp cap and allowed to stir for 30 min in the dark. O_2 was then purged into the Pyrex vessel to achieve an O_2 atmosphere of pressure 0.1 MPa. The reaction mixture was then illuminated by the light source, under magnetic stirring at 800 rpm. Upon reaction completion, the catalyst was separated from the reaction mixture by centrifugation. The product identities were confirmed by comparison of the gas chromatography (GC) retention times with that of standard samples. The products were then quantitatively analyzed through a GC (Agilent 7890A) equipped with a flame ionization detector (FID) and Agilent Technology 19091J-413 capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 mm) using high-purity N_2 as the carrier gas and chlorobenzene as the internal standard. The standard analysis conditions are: injector temperature 250 °C, detector temperature 300 °C, column temperature ramped from 50 °C to 300 °C with a rate of 20 °C min⁻¹.

To characterize the metal oxide catalysts, the following techniques were used. The crystal phases of the metal oxide catalysts were determined by powder X-ray diffraction (XRD). The Brunauer–Emmett–Teller (BET) surface area was measured with an ASAP 2020 apparatus (Micromeritics Instrument Corp.). Temperature programmed desorption with CO₂ and NH₃ was used to identify the strength and quantity of Brønsted acid and base sites on the metal oxide catalysts. The morphologies of the samples were examined by transmission electron microscopy (TEM, JEOL JEM-2100F). UV-visible diffuse reflectance spectroscopy was used to investigate the optical properties of the dyes and metal oxide samples by a UV-vis spectrophotometer (scan-lambda 750) with barium sulfate as the reference, which was subsequently transformed to the absorption spectra according to the Kubelka-Munk relationship. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD system with a monochromatized Al K α source ($h\nu = 1486.6$ eV). A takeoff angle of 0° relative to the surface normal was used to sample the maximum surface depth. Energy calibration was referenced to the C 1s peak at 284.8 eV.

To investigate the catalytic properties of the metal oxide catalysts, the following techniques were employed. Cyclic voltammetry was used to identify the influence of the metal oxide catalysts on the oxidation potential of the reactant. Time resolved photoluminescence was used to investigate the electron transfer mechanism between the dye and the metal oxide catalysts. First principles calculations were used to characterize the electronic properties of the metal oxide catalysts at the surface, as well as their interactions with the reactant and oxygen. Although many γ -phase Al₂O₃ models have been proposed, the one propositioned by Digne et al.⁸² was used due to its popularity and predictive power with respect to the γ -Al₂O₃ surface.

3.2 Gas Chromatography

Gas chromatography is a technique for separating and analyzing the composition of chemicals in a sample mixture.⁸³⁻⁸⁵ A gas chromatograph (GC) consists of the following main components; the *inlet* into which the sample mixture is injected, the *column* in which the mixture is separated into its components, and the *detector* that converts the received chemicals into electronic signals (**Figure 3.1**).^{86,87} The most crucial process occurs in the column, which is filled with a specific material called the *stationary phase*. The mixture is carried through the column via a carrier gas, called the *mobile phase*, and the rate of travel of each individual component depends largely on its chemical and physical properties, as well as its interaction with the stationary phase. This causes the components of the sample mixture to exit the column and enter the detector at different times. These exit times are used to differentiate the different components of the sample mixture. They can also be altered by varying other factors such as the flow rate of the mobile phase, the length of the column, the temperature of the column oven and its ramp rate, in order to achieve a better separation of the components.

Figure 3.1 Simplified diagram of a gas chromatograph.

Figure 3.2 Photograph of a gas chromatograph.

3.2.1 Inlet

In our GC, the inlet is composed of a *S/SL (split/splitless) injector* (**Figure 3.3**),⁸⁷ which comprises a syringe passing through a septum to introduce the sample mixture to a heated *chamber* (250 °C), where the mixture is vaporized. *Split* refers to a mode in which part of the now gaseous sample mixture is vented out of the chamber; only a fraction is carried into the column by the mobile phase. This mode is favoured for sample mixtures with high concentrations of the individual components (>0.1 %). On the other hand, *splitless* refers to a mode in which all of the sample mixture is carried into the column by the mobile phase. This is in order to facilitate detection of trace amounts of components (<0.01 %). In order to remove heavier components that would contaminate the column, the split valve would open after a certain amount of time to vent these components. This splitless time can be controlled to improve the detection signals; using a shorter time can reduce the tailing but also result in smaller signals, while using a longer time can give a better signal but lead to an increase in tailing.

Figure 3.3 Picture of a split/splitless inlet. Reproduced with permission from Agilent Technologies, Inc.

Other types of inlets are the on-column inlet and programmed-temperature-vaporizing (PTV) injector, which introduce the sample mixture at lower temperatures to prevent decomposition, as well as the purge-and-trap inlet which enable the separation and analysis of volatiles from an aqueous solution by passing an inert gas through it.

3.2.2 Detector

The flame ionization detector (FID) is the detector of choice for our GC (**Figure 3.4a**). This is one of the most popular choices for detectors in the GC. The FID comprises detector electrodes and chimney containing a hydrogen-fueled fire (**Figure 3.4b**). The purpose of the fire is to pyrolyze compounds containing *carbon*, which would then form cations and electrons. This would result in a current being detected by the electrodes, which would be seen by the user as a peak in the chromatogram.⁸⁸ The FID is particularly suitable for this research in which the analysis of aromatic organic compounds is crucial. Other advantages of the FID detector include its ability to detect a wide range of compounds over a good range of concentrations, and its low detection limits (in the order of pictograms per seconds for precise quantification of sample components). The FID has its limitations, which are its inability to detect water and its tendency to destroy the sample analytes upon analysis; however, these are not issues with this research, which does not require water detection nor the preservation of analytes post-reaction.

Figure 3.4 a) Pictures of a flame ionization detector and b) the chimney it is housed in. Reproduced with permission from Agilent Technologies, Inc.

3.2.3 Column

The type of column used in our GC is the *capillary column* (**Figure 3.5**). A capillary column is made up of a *tubing* containing the *stationary phase*. The capillary column used by us is of the dimensions $30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ mm}$, with a tubing is made of stainless steel to withstand high temperatures and a stationary phase of polysiloxanes due to their stability and versatility.

The column of a GC is typically housed in an oven that controls its temperature.⁸⁷ The temperature of the column affects the rate of travel of the sample components, which in turn affects their separation. The temperature pattern throughout the separation process is known as the *temperature program*, and tend to *ramp* up the temperature from an *initial temperature* to a *final temperature*. Higher temperatures tend to lead to poorer separation; when the temperature of the column increases, the rate of travel of the analytes increases, which reduces their interaction with the column. However, lower temperatures may render the separation process time-costly as analytes take a longer time to exit the column. Therefore an optimization between the quality and duration of separation is necessary. In our column, the column temperature ramped from $50\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$ at a rate of $20\text{ }^{\circ}\text{C min}^{-1}$.

Figure 3.5 Picture of a capillary column in the oven.⁸⁷ Reproduced with permission from Reference 88. Copyright 2010, Agilent Technologies, Inc.

3.3 Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) used to characterize the crystal structure of the metal oxides by irradiation the metal oxides with X-ray beams at various angles and then measuring the angles and intensities of the diffracted beams.⁸⁹ The X-ray beams are diffracted by the lattice planes, which are separated by a lattice spacing (d) (**Figure 3.6**). The diffracted beams undergo constructive and destructive interference such that the difference in their path lengths is a multiple integer of the wavelength ($n\lambda$). The X-ray diffraction spectrum is plotted as the intensity of the diffracted beams versus the angle at which they are measured. This constitutes the Bragg's Law:⁹⁰ $2d\sin\theta = n\lambda$, where d is the lattice spacing of the crystal plane present in the unit cell of the metal oxide, θ is the angle at which the diffracted beam is measured, n is an arbitrary integer, and λ is the wavelength of the X-ray beam.

Figure 3.6 Schematic of X-ray diffraction.

The specific angles of the peaks observed in the X-ray diffraction spectrum correspond to specific lattice planes, and each crystal structure has a characteristic collection of lattice planes. Through this, the crystal structure can be identified from its diffraction pattern.⁹¹

3.4 Adsorption Studies

3.4.1 Brunauer–Emmett–Teller (BET) Surface Area

Adsorption studies are extremely crucial for characterizing the surface of the metal oxides used. To determine the specific surface area of the metal oxides, nitrogen adsorption measurements combined with Brunauer–Emmett–Teller (BET) theory were performed.⁹² Nitrogen is chosen because it is an inert and non-corrosive gas. The BET theory is an add-on to the Langmuir theory, addressing multilayer adsorption (**Figure 3.7**)⁹³ where the latter addresses only single layer adsorption. The BET theory is based on the following paradigms:⁹⁴

1. Gas molecules physically adsorb on a solid and form an indefinite amount of layers.
2. No interaction exists between the adsorption layers.
3. The Langmuir theory is applicable to each individual layer.

Figure 3.7 BET model depicting the multi-layer adsorption of nitrogen molecules.

When performing nitrogen adsorption studies to determine the surface area of the material, the quantity of adsorbed gas molecules v is measured at different temperatures, and a BET plot of $\frac{1}{v[(\frac{p_o}{p})-1]}$ vs $\frac{p}{p_o}$ is generated. In the range of $0.05 < \frac{p}{p_o} < 0.35$, the plot would be linear and the quantity of gas molecules adsorbed as a monolayer of the material's surface v_m can be obtained from the gradient via the following equation:

$$\frac{1}{v[(\frac{p_o}{p})-1]} = \frac{c-1}{v_m c} \left(\frac{p}{p_o}\right) + \frac{1}{v_m c}$$

Where p and p_o are the equilibrium and the saturation pressure of adsorbed gas molecules, v and v_m are the quantity of total adsorbed gas molecules and that in the monolayer, and c is the BET constant, which can be expressed as:

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

Where E_1 is the heat of adsorption for the 1st layer of gas molecules, while E_L is that for the subsequent layers.

Having obtained the quantity of gas molecules adsorbed as a monolayer of the material's surface v_m , the specific surface area S_{BET} can be calculated as:

$$S_{BET} = \frac{(v_m N s)}{V m}$$

Where N is Avogadro's constant, s is the adsorption cross-section of nitrogen, V is the molar volume of nitrogen, and m is the mass of the material.

3.4.2 Temperature Programmed Desorption (TPD)

Temperature programmed desorption is a technique that probes the surface properties of a material through the adsorption and subsequent desorption of gas molecules with increasing temperature. Different gas molecules can be used to probe different characteristics of the material's surface due to their selective adhesion to certain surface sites. In this thesis, CO_2 gas molecules was used to probe Brønsted base sites on the surface, while NH_3 gas molecules was used to probe Brønsted acid sites. During the initial adsorption phase, gas molecules form a physical or chemical bond with the surface, and when the temperature increases, energy is transferred to the adsorbed gas molecules, causing them to leave the surface. The desorbed gas molecules are detected by a mass spectrometer and translated into peaks on the temperature desorption spectrum (TDS, **Figure 3.8**). Each peak is typically interpreted as one type of surface binding site, and its corresponding desorption temperature and integral provides information about its binding strength and quantity, respectively. The stronger the bond, the more energy it takes for the gas molecules to desorb.

Figure 3.8 Temperature Desorption Spectrum.

To obtain the activation energy of desorption, the desorption process is first understood through the Arrhenius equation:

$$r(\sigma) = -\frac{d\sigma}{dt} = v(\sigma)\sigma^n \times e^{-\frac{E_{act}(\sigma)}{RT}}$$

Where $r(\sigma)$ is the desorption rate as a function of the surface coverage σ , n is the order of desorption, $v(\sigma)$ is the pre-exponential factor as a function of σ , $E_{act}(\sigma)$ is the activation energy of desorption as a function of σ , R is the gas constant and T is the temperature. As this is difficult equation to solve due to the many variables that are functions of the surface coverage σ , the equation is typically simplified by making the following assumptions:⁹⁵

1. $E_{act}(\sigma)$ and $v(\sigma)$ are independent of σ .
2. The rate of heating is linear.
3. No gas molecules are re-adsorbed during desorption.

This gives the simplified Arrhenius equation:

$$r(t) = -\frac{d\sigma}{dt} = v_n\sigma^n \times e^{-\frac{E_{act}}{RT}}$$

Where $r(t)$ is the desorption rate, n is the order of desorption, $v(\sigma)$ is the pre-exponential factor, $E_{act}(\sigma)$ is the activation energy of desorption, R is the gas constant and T is the temperature.

3.5 Time Resolved Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a technique that measures the luminescence emitted from a material following light excitation. This exploits the ability of certain materials to form electron-hole pairs upon photon absorption, and the photons emitted upon electron-hole recombination constitutes the luminescence.^{96,97} Generally, the energy of the photoluminescence can be interpreted as the difference between the ground and excited state that received the photoexcited electron, though the underlying mechanism tends to be more complex with many-body systems, i.e., semiconductors.^{98,99}

In time resolved photoluminescence spectroscopy (TRPL), the excitation is conducted with a light pulse and the photoluminescence decay with time is recorded, such that the lifetime of the excited carriers can be measured.¹⁰⁰ In a system comprising two interacting materials, i.e., Al_2O_3 and dye, TRPL can be used to trace the effect of Al_2O_3 lifetime of the excited state of the dye (**Figure 3.9**). This can provide some understanding on the electron transfer mechanism;¹⁰¹ a greater rate of decay indicates a more rapid quenching of the excited state of the dye, which in turn suggests that electron transfer occurs from the excited dye to Al_2O_3 .

Figure 3.9 Time-resolved photoluminescence spectrum.

3.6 Cyclic Voltammetry

Cyclic voltammetry is a technique that investigates the electrochemical properties of a sample by measuring the current flow generated when the potential of the working electrode is ramped up linearly with time to a set value (cathodic current), and then ramped back down to the initial value (anodic current).¹⁰²⁻¹⁰⁴ This process requires at least two electrodes, the working electrode and the counter electrode in order to enable the current flow. The potential of the working electrode is measured against that of the reference electrode, which is a half cell with a pre-determined reduction potential. Thus, a total of three electrodes are required (**Figure 3.10**) A cyclic voltammogram is then generated by plotting the current versus the potential. Peaks generated under positive potential correspond to oxidation of the sample, and peaks generated under negative potential correspond to reduction of the sample. Based on the observation of peaks, cyclic voltammograms can be classified into two simple types: one with reversible couples, and one with irreversible couples. In the former, the original state of the sample can be recovered with the reverse potential scan such that:¹⁰³

$$\frac{i_{pa}}{i_{pc}} = 1$$

Where i_{pa} is the current corresponding to the anodic peak, and i_{pc} is the current corresponding to the cathodic peak.

ΔE_p , which is the difference between the potentials corresponding to the cathodic (E_{pc}) and anodic peaks (E_{pa}) may provide information on the polarization and diffusion of the sample:

$$\Delta E_p = |E_{pc} - E_{pa}|$$

In irreversible reactions, the magnitudes of the currents corresponding to the cathodic and anodic peaks are not equal:

$$\frac{i_{pa}}{i_{pc}} \neq 1$$

Where i_{pa} is the current corresponding to the anodic peak, and i_{pc} is the current corresponding to the cathodic peak.

Figure 3.10 Three electrodes cell, comprising the counter electrode (C.E.), the reference electrode (R.E.), and the working electrode (W.E.).

Chapter 4

Al₂O₃ and Dye Surface Complex System for Photocatalytic Organic Transformation of Benzylalcohols to Benzaldehydes

Using sunlight as a driving force for organic reactions constitutes a green and sustainable strategy for organic synthesis. The types of organic transformations achievable have been extended with the concept of dual catalysis, in which a photosensitizer is coupled with another type of catalyst in order to enable more sophisticated reactions. It is theorized that Al₂O₃, with its unique surface characteristics, can be coupled with a photosensitizer to enable other difficult organic transformations. In this chapter, it is discovered that Al₂O₃ surface complexation could also be used to induce an immense increase in the selective photo-oxidation of different benzylalcohols in the presence of different dyes and O₂. The mechanism behind this system involves the surface complexation of benzylalcohol (BnOH) with the Brønsted base sites on Al₂O₃, which results in the decrease of its oxidation potential and an upshift in its HOMO for electron abstraction by the dye. The surface complexation of O₂ with Al₂O₃ also activates the adsorbed O₂ for receiving electrons from the photoexcited dyes. This discovery brings forth a new understanding on utilizing surface complexation mechanisms between the reactants and earth abundant materials to effectively achieve a wider range of photoredox reactions.

* Leow, W. R.; Ng, W.; Peng, T.; Liu, X.; Li, B.; Shi, W.; Lum, Y.; Wang, X.; Lang, X.; Li, S.; Mathews, N.; Ager, J. Sum, T. C.; Hirao, H.;* Chen, X.* "Al₂O₃ Surface Complexation for Photocatalytic Organic Transformations" *J. Am. Chem. Soc.*, **2017**, 139 (1), 269–276.

4.1 Introduction

Photoredox catalysis constitutes an exciting strategy to achieve difficult organic transformations towards the production of industrially-valuable products under mild conditions and with less toxic reagents^{1,2}. Selective aerobic photocatalytic organic transformations, in particular, have garnered much interest as it utilizes the molecular oxygen in air, a clean, environmentally friendly, and inexpensive resource. A popular example is the selective oxidation of aromatic alcohols to aldehydes, an important method for converting raw materials into fine chemicals³⁻⁵ especially in the flavor and fragrance industry^{6,7}. Typically, stoichiometric amounts of toxic oxidants are required during synthesis,⁸⁻¹¹ but recent research has shown that the reaction can also be achieved with visible light and oxygen, through the use of an appropriate catalyst. This would help to minimize any deleterious effects on both human health and the environment.

As we have mentioned in the first hypothesis, for such selective aerobic photocatalytic organic transformations, reaction can proceed only if the oxidation potential of the photocatalyst is greater than that of the organic reactants²⁰. A common strategy to fulfill this condition is to use wide band gap semiconductors²¹ such as TiO₂^{3,6,22-28} or Nb₂O₅^{29,30}, which are unable to access the longer wavelength range of the solar spectrum. Another strategy is to redesign the photocatalyst by changing the cation^{20,31-33} or the ligands of transition metal complexes to tune the reduction potential,^{20,34} which would require unique photocatalysts to be synthesized for specific reactions. Therefore, in this chapter, we strive to reduce the oxidation potential of the reactant through complexation with Al₂O₃, which would render it susceptible to oxidation or reduction by photocatalysts with smaller oxidation potentials. This is demonstrated through the selective aerobic photocatalytic oxidation of benzylalcohols to benzaldehydes.

4.2 Experimental Methods

4.2.1 Preparation and Characterization of Al₂O₃

All solid catalysts were purchased from Sigma Aldrich and Alfa Aesar and used without further modification. The synthesized Al₂O₃ was prepared by solid state reaction, in which 7.5 g of aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O) dissolved in 50 ml deionized water was adjusted to pH 7.0 with NH₃·H₂O solution, dried, and then calcined at 600 °C. Powder X-ray diffraction (XRD) was recorded by a Bruker-AXS X-ray diffractometer with Cu K α irradiation (λ = 1.5418 Å). The morphologies of the samples were examined by scanning (SEM, JEOL-JSM-7600F) and high-resolution transmission electron microscopy (HRTEM, JEOL-JEM-2100F). The Brunauer–Emmett–Teller (BET) surface area was measured with an ASAP 2020 apparatus (Micromeritics Instrument Corp.). UV-visible diffuse reflectance spectroscopy was used to measure the optical properties of Al₂O₃ with barium sulfate as the reference and transformed to the absorption spectra according to the Kubelka-Munk relationship. The CO₂-TPD was performed on the Auto Chem 2920 (USA) apparatus. 0.10 g of the sample was loaded in a U-shaped quartz tube, heated at 550 °C for 1 h in helium flow and then cooled to 40 °C, in order to saturate the sample with CO₂. The CO₂-TPD spectrum was then measured in the temperature range of 40–600 °C at a constant heating rate of 10 °C min⁻¹.

4.2.2 Reaction and Post-Reaction Analysis

All reactants and catalysts were purchased from Sigma Aldrich and used without further purification, and all solvents were purchased from Fisher Chemical. In a typical reaction, 50 mg of Al₂O₃, 0.5 μ mol of Ru(bpy)₃Cl₂, and 0.1 mmol of BnOH were added to 5 mL of CH₃CN in a Pyrex vessel and allowed to stir for 30 min in the dark. O₂ was then purged into the Pyrex vessel to achieve an O₂ atmosphere of pressure 0.1 MPa. The reaction mixture was then illuminated by the 7 W white light household LED, which is a cheap and widely available source of light, for 12 h unless otherwise stated, the

irradiating wavelength range of which was measured to be 400-700 nm, with two maxima at 450 and 550 nm, under magnetic stirring at 800 rpm. Upon reaction completion, the Al₂O₃ particles were separated from the reaction mixture by centrifugation. The product identities were confirmed by comparison of the gas chromatography (GC) retention times with that of standard samples. The products were then quantitatively analyzed through a GC (Agilent 7890A) equipped with a flame ionization detector (FID) and Agilent Technology 19091J-413 capillary column (30 m × 0.32 mm × 0.25 mm) using high-purity N₂ as the carrier gas and chlorobenzene as the internal standard. The standard analysis conditions are: injector temperature 250 °C, detector temperature 300 °C, column temperature ramped from 50 °C to 300 °C with a rate of 20 °C min⁻¹.

4.2.3 Theoretical Simulation of the Dyes' Energy Structure

The Gaussian09 package was used for the DFT calculation of the dye molecules. The B3LYP functional with 6-31G* basis set is used for the calculations. For Rose Bengal, the iodide atoms were treated with the SDD basis set. To take the solvation effect into account, the self-consistent reaction field (SCRF) approach was used and the solvent involved is always acetonitrile¹⁰⁵⁻¹⁰⁷. The energy level of Rhodamine B in vacuum is very low due to its positive charge (no counter ion is added to the system). The HOMO-LUMO gaps are almost always larger than the S₀S₁ transition energy predicted by TDDFT. This is the most significant for Ru(bpy)₃²⁺ as it is cationic and its electronic transition is MLCT, which tends to deviate a lot from its HOMO-LUMO gap.

4.2.4 Cyclic voltammetry

The Al₂O₃ modified electrode was fabricated according to procedures present in literature. Basically, Al₂O₃ paste was deposited using a simple doctor-blade technique on fluorine-doped stannic oxide coated glass (sheet resistance of 15 Ω/sq., Nippon Sheet Glass Co., Ltd., Japan). The resulting layer was dried in air at room temperature and heated at 450 °C for 1 hour before cooling to room temperature. Cyclic voltammetry was

carried out using a CHI 660D electrochemical workstation (CH Instruments, Inc., Austin, USA). A three-electrode configuration was used for the measurement of cyclic voltammetry: the as-prepared Al₂O₃ modified FTO glass as the working electrode, platinum wire as the counter electrode, and an Ag/Ag⁺ electrode as the reference electrode. A 0.1 M solution of tetra-n-butylammonium hexafluorophosphate (TBAPF₆) in CH₃CN was used as the supporting electrolyte. Ferrocene was employed as internal standard. A glassy carbon electrode was used as working electrode for the measurement of oxidative potential of BnOH.

4.2.5 Theoretical Simulation of the BnO-Al₂O₃ Surface Complex

All calculations are based on the γ -phase Al₂O₃ model proposed by Digne et al.⁸². A slab with the (110) facet exposed is created to model BnOH adsorption. The dimensions of the slab are (16.826Å*16.136Å*25.000Å). Next, periodic boundary condition calculations were conducted with VASP computational packages¹⁰⁸⁻¹¹¹. The PBE functional and PAW method were used for calculation and only the Γ point is chosen for Brillouin zone sampling¹⁰⁵⁻¹⁰⁷. The HOMO level of the free BnOH molecule is determined from the vertical ionization energy, which is calculated by the Gaussian09 package using PBE functional with 6-31+G* basis set. The vacuum level is used to locate the absolute energy level.

4.2.6 Time-Resolved Photoluminescence (TRPL) Measurement

A pump wavelength of 400 nm was used for the TRPL measurement, which originates from the frequency doubled 800 nm laser pulses generated from a Coherent Libra Regenerative Amplifier using a Beta Barium Borate (BBO) crystal. The resultant luminescence signal was collected and subsequently dispersed by a DK240 1/4-m monochromator with 300 g mm⁻¹ grating. The transient photoluminescence signal was then resolved by an Optronis Optoscope streak camera system, which possesses an ultimate temporal resolution of about 10 ps when operating at the fastest scan speed.

4.3 Outcome

4.3.1 Al₂O₃ and Ru(bpy)₃²⁺ Surface Complex System for the Selective Photocatalytic Oxidation of Benzylalcohols under Visible Light

In this chapter, we successfully achieved the visible-light-driven oxidation of benzyl alcohol (BnOH, **1a**) to benzaldehyde **2a** through the combined use of Al₂O₃ and Ru(bpy)₃²⁺ in the presence of molecular O₂ (**Figure 4.1a**). The reaction was achieved under mild conditions such as irradiation with a 7 W household white light LED and O₂ as the oxidant. Unless otherwise stated, the Al₂O₃ used is the commercially-available [Aldrich 517747]. The surface complex system comprising Al₂O₃ and Ru(bpy)₃²⁺ enabled high conversion and selectivity 79.4(±4.4)% and 82.6(±4.9)% after 12 h, respectively. Negligible conversion of **1a** in the dark and under nitrogen atmosphere (**Figure 4.1b**) indicated that (1) the reaction proceeds via a photocatalytic pathway, and (2) O₂ was essential for the transformation of BnOH, which suggests that O₂ serves as a sacrificial electron acceptor that receives two electrons and two protons from BnOH to form benzaldehyde. The initial BnOH conversion generally increased with the amount of Al₂O₃ used, but the extent of increment becomes less significant for larger amounts of Al₂O₃ (**Figure 4.1c**).

The phenomenon can also be extended to other commercial Al₂O₃ and Al₂O₃ synthesized via solid state reaction, but not for the non-mesoporous commercial Al₂O₃ [Aldrich 718475] (**Figure 4.1d**). The basic Al₂O₃ [Alfa Aesar 11503] showed higher conversion compared to the neutral [Alfa Aesar 11502] and acidic Al₂O₃ [Alfa Aesar 11501], which indicates the importance of Brønsted basicity towards the reaction. This will be further investigated in **Section 4.3.3**. It is interesting to note that the use of Al₂O₃ or Ru(bpy)₃²⁺ alone led to only trace conversions of BnOH (**Figure 4.1e**). The phenomenon appears to be exclusive to Al₂O₃; with other metal oxides such as SiO₂ and MgO, only negligible **1a** conversions were observed. The characterizations of the metal oxides used can be found in **Figure 4.2-4** and **Table 4.1**.

Figure 4.1 a) Visible light driven oxidation of benzylalcohol to benzaldehyde with molecular O₂. b) The importance of light and O₂. c) Initial conversion (1 h) versus the amount of Al₂O₃ used. d) The extensiveness of the Al₂O₃ and Ru(bpy)₃²⁺ dual surface complex system towards different commercial Al₂O₃ products. e) The exclusivity of the reaction towards the Al₂O₃ and Ru(bpy)₃²⁺ combined surface complex system. Reaction conditions: 0.1 mmol BnOH, 0.5 μmol Ru(bpy)₃Cl₂, 50 mg Al₂O₃, 5 mL CH₃CN, 0.1 MPa O₂, 7 W white-light LED irradiation for 12 h. Conversion was determined by GC analysis using chlorobenzene as the internal standard.

Figure 4.2 X-ray diffractograms of **a)** mesoporous Al₂O₃ [Aldrich 517747], **b)** post-reaction mesoporous Al₂O₃ [Aldrich 517747], **c)** SiO₂, **d)** MgO, **e)** acidic Al₂O₃ [Alfa Aesar 11501], **f)** neutral Al₂O₃ [Alfa Aesar 11502], **g)** basic Al₂O₃ [Alfa Aesar 11503], **h)** synthesized mesoporous Al₂O₃, **i)** non-mesoporous Al₂O₃ [Aldrich 718475].

Figure 4.3 a) and b) TEM images and c) SAED pattern of mesoporous Al₂O₃ [Aldrich 517747].

Figure 4.4 SEM images of a) mesoporous Al₂O₃ [Aldrich 517747], b) post-reaction mesoporous Al₂O₃ [Aldrich 517747], c) SiO₂, d) MgO, e) acidic Al₂O₃ [Alfa Aesar 11501], f) neutral Al₂O₃ [Alfa Aesar 11502], g) basic Al₂O₃ [Alfa Aesar 11503], h) synthesized mesoporous Al₂O₃, i) non-mesoporous Al₂O₃ [Aldrich 718475].

Figure 4.5 Spectral irradiance and absorbance of the key players in the reaction. **a)** Emission spectrum of the LED light source. Diffuse-reflectance spectrum of **b)** BnOH, **c)** Al₂O₃, and **d)** the dyes used in conjunction with Al₂O₃ during the photocatalytic BnOH oxidation.

Table 4.1 BET surface areas, BJH Desorption cumulative volumes and BJH desorption average pore diameter of the metal oxides used.

Entry	Sample	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Size (Å)
1	Mesoporous Al ₂ O ₃ [Aldrich 517747]	332	0.460	25.5
	Post-Reaction			
2	Mesoporous Al ₂ O ₃ [Aldrich 517747]	223	0.369	27.9
3	SiO ₂	501	1.01	33.9
4	MgO	11.3	0.0489	132
5	Acidic Al ₂ O ₃ [Alfa Aesar 11501]	164	0.244	23.0
6	Neutral Al ₂ O ₃ [Alfa Aesar 11502]	159	0.253	24.4
7	Basic Al ₂ O ₃ [Alfa Aesar 11503]	138	0.254	27.1
8	Synthesized mesoporous Al ₂ O ₃	165.4	0.386	8.07
9	Non-mesoporous Al ₂ O ₃ [Aldrich 718475]	95.9	0.252	70.7

4.3.2 Generality and Tunability of the Al₂O₃ and Dye Surface Complex System

The generality of this Al₂O₃ and Ru(bpy)₃²⁺ surface complex system was investigated with 10 other benzyl alcohol derivatives (**1a-k**); similarly high conversions (52.5-88.6%, with most >75.0%) were obtained (**Figure 4.6**). The formation of the aforementioned BnO-Al₂O₃ surface complex can be attributed to the presence of strong Brønsted base sites on the surface of Al₂O₃. It can be seen that the 2-methoxybenzyl alcohol **1c** shows a drop in conversion relative to 4-methoxybenzyl alcohol **1d**, possibly because the methoxy group in the ortho position in the former reactant provided greater steric hindrance around the O-H group. Thus, the benzylic O-H interaction with the Al₂O₃ surface should be a crucial step in the reaction. It has been reported that the photooxidation of BnOH with Ru(4,4'-CO₂CH(CH₃)₂-bpy)₃²⁺ and the diazonium salt of 2-aminobenzophenone requires a sacrificial organic base like collidine (2,4,6-trimethylpyridine) that accepts a proton from benzylic O-H^{20,34}. Hence the dissociation of benzylic O-H should arise from the basic sites on the surface of the Al₂O₃.

Figure 4.6 Conversion of different benzyl alcohols by Ru(bpy)₃²⁺ with and without Al₂O₃. Reaction conditions: 0.1 mmol BnOH, 0.5 μmol Ru(bpy)₃Cl₂, 50 mg Al₂O₃, 5 mL CH₃CN, 0.1 MPa O₂, 7 W white-light LED irradiation for 12 h. Conversion was determined by GC analysis using chlorobenzene as the internal standard.

The phenomenon can also be observed with a large variety of dyes of different moieties. While none of the dyes were able to oxidize BnOH without Al₂O₃, most were achieved significant conversion with Al₂O₃ (**Figure 4.7a**). The extent of conversion depends on the compatibility of the dye's excitation wavelength with that of the LED. Ru(bpy)₃²⁺ and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), with excitation wavelengths between 450-550 nm, yielded high conversions of 79.4(±4.4)% and 82.2(±11.1)%, respectively. Rose Bengal and Rhodamine B showed significant conversions of 64.5(±4.6)% and 36.2(±2.6)%, respectively, but their lack of stability undermines their photocatalytic activity. 5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin (TMPP), with excitation wavelength at 418 nm, showed substantial conversion of 50.5(±0.8)%. 9-Anthracenecarboxylic acid (ACA), with absorbance peaks in the range of 300-400 nm that is far from the wavelengths of the LED, yielded a low conversion of 23.0(±1.7)%. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA), which absorbs light below 365 nm, showed little increment in conversion compared to the case with Al₂O₃ only. From this, we can see that the Al₂O₃ can be coupled with a variety of dyes to induce the photocatalytic transformation of BnOH, and that the extent of conversion depends on the compatibility between the wavelengths of the dye and the LED.

To further demonstrate the aforementioned theory, when the light source is switched to one with a wavelength range that is suitable for absorption by the ACA (350-750 nm), the combined Al₂O₃-ACA surface complex system was able to effect a significant degree of conversion, i.e. 78.0% in 2 h, even though ACA by itself was only able to achieve a low conversion of 27.3% (**Figure 4.7b**). The Ru(bpy)₃²⁺ and Al₂O₃ surface complex system showed a higher conversion than Degussa P25 under illumination by a light source of the 450-750 nm wavelength range, and the PTCDA and Al₂O₃ surface complex system showed higher conversion under the 490-750 nm wavelength range (**Figure 4.7c**). By selecting a dye with an appropriate excitation wavelength, higher wavelengths of light can easily be accessed by the Al₂O₃-dye surface complex system.

Figure 4.7 **a)** The extensiveness of the Al₂O₃-dye surface complex system towards dyes of different moieties. **b)** The efficacy of Al₂O₃ and ACA dual surface complex system under a wavelength range suitable for ACA absorption (350-750 nm). **c)** Efficacy of Al₂O₃ and dye dual surface complex system vs that of TiO₂ at higher wavelengths. Reaction conditions: 0.1 mmol BnOH, 0.5 μmol Ru(bpy)₃Cl₂, 50 mg Al₂O₃, 5 mL CH₃CN, 0.1 MPa O₂, 7 W white-light LED irradiation for 12 h. Conversion was determined by GC analysis using chlorobenzene as the internal standard.

4.3.3 Complexation with the Brønsted base sites the Al₂O₃ Surface Reduces the BnOH Oxidation Potential

The importance of Brønsted base sites towards the reaction was revealed by the decrease in conversion with increasing amounts of acetic acid added (**Figure 4.8a**), which suggests that acetic acid competes with BnOH for chemisorption on the Brønsted

base sites of Al₂O₃ (**Figure 4.8b**). The basic nature of the Al₂O₃ surface was probed through temperature-programmed desorption of CO₂ (CO₂-TPD) from 100 to 600 °C (**Figure 4.8c and d**). Three peaks could be observed, with maxima lying at about 87, 280, and 430 °C, corresponding to the desorptions of weakly, moderately, and strongly bound CO₂, respectively. The highest peak was at 430 °C, which is suggestive of the abundance of strong Brønsted base sites on the surface of Al₂O₃ that could deprotonate the BnOH. This appears to be consistent with existing reports that the Brønsted base sites on the Al₂O₃ surface could enable the chemisorption of alcohols to form alkoxides ^{15,112}.

Figure 4.8 a) The quenching of conversion with the addition of acetic acid. b) Schematic of acetic acid competing with BnOH for the active sites on the Al₂O₃ surface. CO₂ temperature programmed desorption (TPD) of c) Al₂O₃, d) SiO₂, and e) MgO.

The importance of BnOH complexation with the Brønsted base sites on the Al₂O₃ surface can be explained by the modification of the BnOH oxidation potential. Cyclic voltammetry conducted on BnOH in CH₃N with a bare glassy carbon electrode showed an irreversible BnOH oxidation peak at around +2.0 V vs Ag/AgCl.³⁴ As the Ru(bpy)₃²⁺/Ru(bpy)₃³⁺ potential in acetonitrile is +1.29 V vs SCE (+1.34 V vs Ag/AgCl),^{20,113} BnOH cannot be oxidized by Ru(bpy)₃³⁺. However, cyclic voltammetry conducted with a Al₂O₃-modified electrode revealed an additional oxidation feature at around +0.63 V vs Ag/AgCl (**Figure 4.9a**), which is within the oxidative potential of Ru(bpy)₃³⁺. This oxidation feature suggests the formation of a chemisorbed BnO-Al₂O₃ surface complex with a lower oxidation potential, which can be easily oxidized by Ru(bpy)₃³⁺ (**Figure 4.10**, step II). No additional oxidation feature was detected in the linear sweep voltammograms conducted with the SiO₂- and MgO-modified electrodes (**Figure 5.5a**), while similar oxidation peaks are detected for the benzyl alcohol derivatives (**Figure 5.5b-d**). The addition of acetic acid, which would compete with BnOH for Brønsted base sites on the Al₂O₃-modified electrode, quenched the oxidation feature at +0.63 V vs Ag/AgCl (**Figure 4.9a**), indicating that the formation of the BnO-Al₂O₃ surface complex occurs through O-H de-protonation by the Brønsted base sites on Al₂O₃.

Figure 4.9 a) Cyclic voltammogram of BnOH with Al₂O₃-modified (red) and bare electrodes (blue), and 40 µl acetic acid (black).

Figure 4.10 Mechanism of the photocatalytic BnOH oxidation by Al₂O₃ and Ru(bpy)₃²⁺.

Figure 4.11 LSV of **a)** BnOH with Al₂O₃ (red), SiO₂ (black) and MgO-modified (blue) electrodes. LSV of **b)** 4-methylbenzyl alcohol, **c)** 4-methoxybenzyl alcohol, and **d)** 4-trifluoromethylbenzyl alcohol with Al₂O₃-modified (red) and bare electrodes (blue).

4.3.4 Theoretical Study on the Surface Energy Structure of the BnO-Al₂O₃ Surface Complex

The reduction of the oxidation potential through surface-complexation is further validated by performing first-principles calculations on free BnOH and BnOH adsorbed on the Al₂O₃ surface. The most widely exposed plane of Al₂O₃, the (110) facet, was simulated based on the Digne model (**Figure 4.12a**)⁸². An isolated complex was used to describe the BnO-Al₂O₃ surface complex approximately, and it was assumed that neighbouring BnOH, Ru(bpy)₃²⁺ and solvent molecules do not exert a large influence on its energy levels. The HOMO of the free BnOH molecule was calculated as -8.46 eV (**Figure 4.12b**). The DOS diagrams for the adsorption of BnOH onto the Al_{III} site before and after O-H dissociation (**Figure 4.12c and d**) show that the PDOS of BnOH is shifted upwards after dissociation. The DOS diagram for the O-H dissociated case also indicates that the two peaks on the left-hand side of the black dashed line with energy > 0 eV are still occupied. The two peaks correspond to occupied localized states arising from the molecule (**Figure 4.12e**), and their energy levels are colored in red in **Figure 4.12b**. The occurrence of these occupied states can be explained via the following; BnOH draws electron density from the surface after O-H dissociation to stabilize its new alkoxide state, which causes it to become electron rich while creating an electron deficiency in a localized area of the surface. The electron gain by the BnOH increases the electron repulsion within the molecule and causes an upward shift in energy level. As the C-H σ -bonds are located at the valence edge, once a hole is generated on the surface by Ru(bpy)₃³⁺ oxidation and transferred to BnOH, this would result in the weakening and subsequent cleavage of the C-H bond to form the benzaldehyde product (**Figure 4.10**, steps III-IV). In this way, Al₂O₃ enables the oxidation of BnOH through the formation of a chemisorbed surface complex that has a lower oxidation potential than Ru(bpy)₃²⁺/Ru(bpy)₃³⁺.

Figure 4.12 a) Theoretical model of Al₂O₃. b) Energy levels of Al₂O₃, free BnOH and the surface complex (values in eV). DOS of c) BnOH physisorbed to the Al_{III} site, and d) chemisorbed via OH dissociation. The dashed line indicates the formation of localized occupied states above the VBM of Al₂O₃. e) Molecular orbitals of the localized states.

4.3.5 Charge-Transfer Dynamics of the Al₂O₃-Ru(bpy)₃²⁺ Surface Complex System

Besides the complexation of BnOH on Al₂O₃, we also addressed the interaction between Al₂O₃ and the photosensitizer by grafting Ru(bpy)₃²⁺ to the surface of Al₂O₃ through –COOH groups, in order to reduce the proximity between the two (**Table 4.2**, Column [b]). As conversion is generally greater for the grafted Ru(bpy)₃²⁺ relative to the ungrafted Ru(bpy)₃²⁺, the interaction of the dye with Al₂O₃ appears to be significant for the reaction. To understand the nature of such an interaction, time-resolved photoluminescence (TRPL) spectroscopy was used to study the charge-transfer dynamics between ungrafted Ru(bpy)₃²⁺ and Al₂O₃. Two samples, Ru(bpy)₃²⁺ as well as Ru(bpy)₃²⁺ adsorbed on Al₂O₃, were photoexcited using 400 nm laser pulses. The resultant TRPL signal occurs as a result of metal-to-ligand charge transfer (MLCT)⁸⁰, generating the excited species Ru(bpy)₃^{2*}, which decays exponentially with time (**Figure 4.13a** and **Table 4.3**) This decay can be either to the recombination of charge carriers to regenerate Ru(bpy)₃²⁺, or the loss of an electron to O₂:

As a similar TRPL lifetime can be observed in the absence of O₂ (**Figure 4.13b**), the recombination pathway appears to be the dominant process. Although the oxidation potential of O₂ is suitable for receiving electrons from Ru(bpy)₃^{2*}, there appears to be little electron transfer between Ru(bpy)₃^{2*} and O₂ in the 300 ns timeframe. The lack of BnOH conversion with MgO and SiO₂ may also be due to negligible electron transfer from Ru(bpy)₃^{2*} to MgO or SiO₂, as the lifetimes of Ru(bpy)₃^{2*} on MgO and SiO₂ are largely similar to that of Ru(bpy)₃^{2*} by itself (**Figure 4.13a** and **Table 4.3**).

Table 4.2 Aerobic oxidation of various benzyl alcohols under visible-light irradiation. Catalyst: [a] 0.5 μ mol Ru(bpy)₃Cl₂ and 50 mg Al₂O₃, ungrafted. [b] 0.5 μ mol Ru(4,4'-CO₂H-bpy)₂(bpy)Cl₂ grafted on 50 mg Al₂O₃.

Entry	Substrate	Product	Conv. [%] ^[a]	Conv. [%] ^[b]
1	1a	2a	79.4	84.1
2	1b	2b	83.0	88.3
3	1c	2c	71.6	74.6
4	1d	2d	88.6	92.2
5	1e	2e	84.4	89.0
6	1f	2f	77.6	88.6
7	1g	2g	88.3	90.4
8	1h	2h	65.9	69.8
9	1i	2i	80.2	81.0
10	1j	2j	52.5	64.3
11	1k	2k	79.1	99.9

Reaction conditions: 0.1 mmol BnOH, 5 mL CH₃CN, 0.1 MPa O₂, 7 W white-light LED irradiation for 12 h. Conversion was determined by GC analysis using chlorobenzene as the internal standard.

Figure 4.13 Decay kinetics of TRPL signals of **a)** Ru(bpy)₃²⁺ and **b)** Ru(bpy)₃²⁺ adsorbed on Al₂O₃.

Table 4.3 Decay lifetimes of the samples measured under ambient and N₂ conditions.

A	Entry	Sample	Atmosphere	Lifetime (ns)
t	1	Ru(bpy) ₃ ²⁺	Ambient	125 ± 2
m	2	Ru(bpy) ₃ ²⁺ + Al ₂ O ₃	Ambient	63 ± 1
o	3	Ru(bpy) ₃ ²⁺ + SiO ₂	Ambient	105 ± 2
s	4	Ru(bpy) ₃ ²⁺ + MgO	Ambient	122 ± 2
p	5	Ru(bpy) ₃ ²⁺	Nitrogen	115 ± 2
h	6	Ru(bpy) ₃ ²⁺ + Al ₂ O ₃	Nitrogen	55 ± 1

e

Meanwhile, it can be seen that under both ambient and N₂ conditions, the lifetime of Ru(bpy)₃^{2*} adsorbed on Al₂O₃ is almost half that of Ru(bpy)₃^{2*} alone (**Figure 4.13b** and **Table 4.3**). This suggests that besides recombination, the electron loss from Ru(bpy)₃^{2*} to form Ru(bpy)₃³⁺ also constitutes a significant process⁸⁰. However, DFT calculations reveal that the CBM of the Al₂O₃ surface is too high at -3.21 eV to receive an electron from Ru(bpy)₃^{2*}. Hence, we hypothesize that electron transfer may not have occurred from Ru(bpy)₃^{2*} to Al₂O₃, but to a O₂ molecule strongly complexed to the surface of Al₂O₃, which may not have been released in the N₂ atmosphere (**Figure 4.14a**).

DFT calculations show that in the gas phase of O₂, the π_x and π_y are half occupied and have same energy level, however, when strongly complexed with Al_{III} site of Al₂O₃, the π_x and π_y becomes energetically inequivalent and lead to a singly occupied π orbital on surface (**Figure 4.14b**). This causes the appearance of a localized vacant band at -5.07 eV (**Figure 4.14c**), which is suitable for accepting electrons from the excited states of all dyes used (**Figure 4.15**) to yield the superoxide O₂⁻ (**Figure 4.10**, steps II-III):

The loss of electrons from Ru(bpy)₃^{2*} would then yield the oxidant species Ru(bpy)₃³⁺, which would drive the reaction forward by removing an electron from the adsorbed BnOH to form an α -carbon radical (**Figure 4.10**, steps III-IV). The overall process is such that, with Al₂O₃ and the photoexcited Ru(bpy)₃^{2*} acting in tandem as a shuttle, an electron transfer is enabled from BnOH to O₂.

Figure 4.14 a) Proposed mechanism of electron transfer between the dye and O₂. b) Occupied and vacant states of the singly occupied π orbital which arose due to O₂ and Al₂O₃ surface complexation. c) Energy levels of Ru(bpy)₃²⁺, Al₂O₃, and O₂.

Figure 4.15 a) Energy levels of the dyes in acetonitrile solvent (PCM model). b) Molecular structures of the dyes used in Figure 1D, and their corresponding molecular orbitals.

4.3.6 Conclusion

The unconventional strategy of utilizing Al₂O₃ surface complexation was employed to modify the oxidation potential of organic reactants, which would enable the oxidation of organic reactants with high oxidation potentials inaccessible to the unassisted photocatalyst. This has been successfully demonstrated through the photocatalytic oxidation of benzyl alcohols to benzaldehydes. High conversion and selectivity can be achieved with the surface complex systems comprising Al₂O₃ and a variety of dyes, but not with these dyes alone. The formation of the chemisorbed BnO-Al₂O₃ surface complex is attributed to the strong Brønsted base sites on Al₂O₃, which accepts protons from benzylic O-H. This causes a shift in the oxidation potential of BnOH, which enhances the ease of subsequent electron and C-H proton abstraction to form benzaldehyde. The surface complexation of O₂ with Al₂O₃ also activates the adsorbed O₂ for receiving electrons from the photoexcited dyes. This discovery may subvert our understanding of the role of Al₂O₃ in photocatalytic reactions. For instance, it may be possible for Al₂O₃ to play a role beyond that of a mere support or scaffold in the performance enhancement in solar hydrogen production⁷⁹ and dye-sensitized solar cells^{114,115}. This discovery brings forth a new methodology of utilizing surface complexation mechanisms between the reactants and earth-abundant materials to effectively achieve a wider range of photoredox reactions.

Chapter 5

Proton Transfer on Brønsted Base Sites for the Photocatalytic Organic Transformation of Phenylboronic Acids to Phenols

In the previous chapter, we have successfully utilized a Al₂O₃-dye dual surface-complex photocatalytic system to the difficult aerobic transformation of benzyl alcohols to aldehydes. In this chapter, we have extended the use of such dual surface-complex photocatalytic system involving earth-abundant metal oxides and dyes to enable the selective photocatalytic oxidation of phenylboronic acids to phenols under visible light and O₂. It was determined that the Brønsted base sites on the metal oxide surface are responsible for enabling the photocatalytic oxidation of phenylboronic acids to phenols. Both the strength and proximity of the Brønsted base sites appear to be extremely important towards driving the reaction. This discovery highlights a significant role that heterogeneous surfaces may play in contributing to photocatalytic organic transformations, thus opening up the possibility of utilizing surface complexation mechanisms between the reactants and earth-abundant materials to bring forth a wider range of photoredox transformations. Such benign and environmentally green organic transformations that utilize sustainable and abundant resources such as sunlight and O₂ are potentially beneficial to industrial conversion of raw materials into valuable products.

Leow, W. R.; Chen, X. D. "Proton Transfer on Brønsted Base Sites for the Photocatalytic Organic Transformations for Phenylboronic Acids to Phenols" (**Manuscript under preparation**)

5.1 Introduction

Photoredox catalysis is a popular strategy for difficult organic transformations, as it shows great promise for the production of industrially-valuable products under mild conditions and with less toxic reagents^{1,2}. In particular, selective aerobic photocatalytic organic transformations have garnered much interest as it utilizes the molecular oxygen in air as a clean, environmentally friendly, and inexpensive oxidant. The mechanism of such reactions typically involves electron transfer to molecular O₂ in order to generate a superoxide anionic radical. It has been reported that such superoxide radicals have Lewis base character, and would therefore react favourable with reactants of Lewis acid character. An example of organic reactants with such Lewis acid character is phenylboronic acids, due to the presence of a vacant p orbital on the boron atom.^{116,117}

In the previous chapter, we have successfully demonstrated the use of an Al₂O₃-dye surface-complex dual photocatalytic system to enable the photocatalytic transformation of benzyl alcohols to aldehydes under mild conditions such as irradiation by a 7 W LED and O₂ as the oxidant. In this chapter, we seek to extend the range of organic transformations achievable through this Al₂O₃-dye surface-complex dual photocatalytic system, such as the oxidative hydroxylation of arylboronic acids to phenols. Phenols are known to be versatile building blocks for products crucial to the chemical and pharmaceutical industries. Therefore, a clean and environmentally friendly strategy for the synthesis of phenols may prove beneficial to the chemical industries. It was discovered that proton transfer from the arylboronic acids to the Brønsted base sites on the Al₂O₃ surface constituted a crucial step in the reaction mechanism.

5.2 Experimental Methods

5.2.1 Reaction and Post-Reaction Analysis

All reactants and catalysts were purchased from Sigma Aldrich and used without further purification, and all solvents were purchased from Fisher Chemical. In a typical reaction, 25 mg of Al₂O₃, 0.5 μ mol of Ru(bpy)₃Cl₂, and 0.1 mmol of 4-ClPhB(OH)₂ were added to 5 mL of CH₃CN in a Pyrex vessel and allowed to stir for 30 min in the dark. O₂ was then purged into the Pyrex vessel to achieve a pressure of 0.1 MPa. The reaction mixture was then illuminated by the 7 W white light household LED for 3 h unless otherwise stated, the irradiating wavelength range of which was measured to be 400-700 nm, with two maxima at 450 and 550 nm, under magnetic stirring at 800 rpm.

Upon reaction completion, the Al₂O₃ particles were separated from the reaction mixture by centrifugation. The product identities were confirmed by comparison of the gas chromatography (GC) retention times with that of standard samples. The products were then quantitatively analyzed through a GC (Agilent 7890A) equipped with a flame ionization detector (FID) and Agilent Technology 19091J-413 capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 mm) using high-purity N₂ as the carrier gas and chlorobenzene as the internal standard. The standard analysis conditions are: injector temperature 250 °C, detector temperature 300 °C, column temperature ramped from 50 °C to 300 °C with a rate of 20 °C min⁻¹.

5.2.2 Materials Characterization

The X-ray diffraction (XRD) patterns were obtained on a Bruker-AXS X-ray diffractometer using Cu K_a radiation (λ =1.54178 Å). The morphologies of the samples were examined by transmission electron microscopy (TEM, JEOL JEM-2100F). UV-visible diffuse reflectance spectroscopy was used to investigate the optical properties of the Al₂O₃ by a UV-vis spectrophotometer (scan-lambda 750) with barium sulfate as the

reference and transformed to the absorption spectra according to the Kubelka-Munk relationship. The surface areas were evaluated by nitrogen adsorption measurements on a Micromeritics ASAP 2010 adsorption analyzer. The CO₂-temperature-programmed-desorption (CO₂-TPD) was performed on Auto Chem 2920 (USA) apparatus. 0.10 g of samples was loaded in the U-shaped quartz tube and heated at 550 °C for 1 h in helium flow and then cooled to 40 °C for the saturation of the catalyst. CO₂-TPD spectra were measured in the temperature range of 40 – 600 °C with a constant heating rate of 10 °C min⁻¹.

5.3 Outcome

5.3.1 Metal Oxide and Ru(bpy)₃²⁺ Surface Complex System for the Selective Photocatalytic Oxidation of Phenylboronic Acids under Visible Light

As mentioned in the previous chapter, we believe that surface complexation mechanisms between the reactants and earth abundant materials can be effectively utilized to achieve a wider range of photoredox reactions. The metal oxide and ruthenium (II) tris(2,2-bipyridine) combined surface complex system was successfully applied to the oxidation of 4-chlorophenylboronic acid (4-ClPhB(OH)₂, **3c**) to phenol (4-ClPhOH, **4c**) in the presence of molecular oxygen and visible light irradiation from a 7 W household white light LED (**Figure 5.1a**). The metal oxides used are commercially available, and their Brønsted base characterization can be found in **Figure 5.1b and c**. The yields of **4c** were much lower when acidic oxides such as B₂O₃ and SiO₂ were coupled with Ru(bpy)₃²⁺, which indicates that Brønsted base sites on the surface of the metal oxides are crucial towards driving the reaction. It is interesting to note that negligible yields were obtained when either metal oxide or Ru(bpy)₃²⁺ was absent. The introduction of acetic acid, which would compete with **3c** for chemisorption on the Brønsted base sites, resulting in an almost complete quenching of the reaction, thus demonstrating the importance of these sites (**Figure 5.1d**).

Figure 5.1 a) Visible light driven oxidation of phenylboronic acid to phenol with molecular O₂. b) Yields of 4-ClPhOH (**3a**) generated by different MO_x-Ru(bpy)₃²⁺ dual surface complex systems. Density of Brønsted base sites on different MO_x surfaces w.r.t. c) surface area and d) mass of MO_x. e) The quenching of reaction with acetic acid. Reaction conditions: 0.1 mmol 4-ClPhB(OH)₂, 0.5 μmol Ru(bpy)₃Cl₂, 25 mg metal oxide, 5 mL DMF, 0.1 MPa O₂, 7 W white-light LED irradiation for 3 h. Conversion and selectivity were determined by GC analysis using diphenyl ether as the internal standard.

To obtain further clues on the contribution of surface Brønsted base sites, the reaction was conducted using different Al₂O₃ coupled with Ru(bpy)₃²⁺. A positive correlation was observed between the yields achieved and the density of strong Brønsted base sites (**Figure 5.2b**, defined here as that corresponding to CO₂-TPD peak maximas

ranging within 240-600 °C), rather than the density of weak (50-239 °C) or all Brønsted base sites (50-600 °C) w.r.t. surface area (**Figure 5.2c and d**). This indicates that the strength and the proximity of the Brønsted base sites are the key factors driving the hydroxylation reaction.

Figure 5.2 a) Density of Brønsted base sites on different Al₂O₃ surfaces w.r.t. surface area. Yields of **2a** generated by Ru(bpy)₃²⁺ coupled with different Al₂O₃, as a function of b) strong, c) weak and d) all Brønsted base sites density w.r.t. surface area. Reaction conditions: 0.1 mmol 4-ClPhB(OH)₂, 0.5 μmol Ru(bpy)₃Cl₂, 25 mg metal oxide, 5 mL DMF, 0.1 MPa O₂, 7 W white-light LED irradiation for 3 h. Conversion and selectivity were determined by GC analysis using diphenyl ether as the internal standard.

The nature of the selective photocatalytic hydroxylation was then investigated through a series of control experiments with Al₂O₃ [Aldrich 517747]. The generality of the Al₂O₃-Ru(bpy)₃²⁺ dual surface complex system was demonstrated through the high yields (56.3-96.0 %) of alcohols (**2a-h**) achieved with 8 boronic acid derivatives (**1a-h**), as shown in **Table 5.1**. It must be noted that the use of Ru(bpy)₃²⁺ by itself resulted in only low yields of alcohols (5.02-23.3%). It can be seen from **Figure 5.3a** that the rate of **4c** production was almost linear with time, but slightly slower in the first hour, possibly due to a slow initiation step, as well as in the last hour, when the reactant concentration has significantly decreased. The photocatalytic and aerobic nature of the reaction was revealed through the negligible yields of **4c** obtained in dark conditions or under nitrogen atmosphere (**Figure 5.3b**). The latter indicates that molecular oxygen should be the oxidant that accepts protons and electrons from **3c** to enable its hydroxylation to **4c**. Next, the amount of water in the reaction system was controlled to understand the origin of the -OH group in the phenol product. As similarly high yields were obtained with both ambient and anhydrous DMF solvents, this suggests that water does not take part in the reaction as a proton or hydroxyl group donor (**Figure 5.3c**). Hence the overall reaction should follow equation (1), which does not involve water as the reactant and generates metaboric acid as the byproduct, rather than equation (2), which involves water and produces boric acid as the byproduct. This appears to be consistent with our aforementioned theory that two or more **3c** molecules are required to be in proximity during the reaction.

Table 5.1 Selective aerobic hydroxylation of various boronic acids under visible-light irradiation.* Catalyst: [a] 0.5 μ mol Ru(bpy)₃Cl₂ only. [b] 0.5 μ mol Ru(bpy)₃Cl₂ and 25 mg Al₂O₃.

Entry	Substrate	Product	Conv. [%] ^[a]	Conv. [%] ^[b]
1	3a	4a	14.6	> 99.9
2	3b	4b	13.4	69.3
3	3c	4c	23.4	56.3
4	3d	4d	17.1	>99.9
5	3e	4e	16.5	67.0
6	3f	4f	5.03	82.2
7	3g	4g	>0.01	75.8
8	3h	4h	5.21	58.4

*Reaction conditions: 0.1 mmol 4-ClPhB(OH)₂, 5 mL DMF, 0.1 MPa O₂, 7 W white-light LED irradiation. Conversion and selectivity were determined by GC analysis using diphenyl ether as the internal standard.

Figure 5.3 a) Yield of 4-ClPhOH versus time. b) The importance of light irradiation and O₂ towards the yield of **4c**. c) The influence of water on the reaction. Reaction conditions: 0.1 mmol 4-ClPhB(OH)₂, 0.5 μ mol Ru(bpy)₃Cl₂, 25 mg metal oxide, 5 mL DMF, 0.1 MPa O₂, 7 W white-light LED irradiation for 3 h. Conversion and selectivity were determined by GC analysis using diphenyl ether as the internal standard.

5.3.2 Generality and Tunability of the Al₂O₃ and Dye Surface Complex System

The Al₂O₃-dye dual surface complex system can be extended to a large variety of dyes of different moieties, such as naphthalene, anthracene, porphyrin, and perylene. The yields of **4c** depend on how closely the excitation wavelength of the photosensitizer corresponds to the LED emission (**Figure 5.4a**). 5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin (TMPP), Ru(bpy)₃²⁺ and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), with excitation wavelengths from 400 to 550 nm, showed extremely high yields of (96.7 $\pm$ 3.30) %, (96.5 $\pm$ 2.47) % and (88.6 $\pm$ 11.7) % under 7 W white light LED irradiation, respectively. 9-Anthracenecarboxylic acid (ACA), with absorbance peaks in the range of 300 to 400 nm, produced a lower yield of (72.0 $\pm$ 9.05) %. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA), which absorbs light below 365 nm, provided only a low yield of (9.59 $\pm$ 7.59) %. Rose Bengal was able to effect significant yield of (50.2 $\pm$ 11.8) %, but its lack of stability prevents it from achieving a

higher yield even though its absorption wavelength is within the range of the LED. It should be noted that TiO₂, which produced negligible yield under 450-750 nm irradiation, is a wide band gap semiconductor with surface Brønsted base sites, and therefore can generate a high yield of >99.9 % by itself under 350-750 nm irradiation (**Figure 5.4a**). From this, it can be seen that the Al₂O₃-dye dual surface complex system can be programmed for compatibility with light sources of different wavelength ranges simply by using a suitable dye.

Figure 5.4 The extensiveness of the Al₂O₃-dye surface complex system towards dyes of different moieties.

5.3.3 Proposed Mechanism

From the aforementioned clues elucidating the nature of the selective photocatalytic hydroxylation of boronic acids, the following mechanism can be proposed. the boron atom of the boronic acid, being a Lewis acid, binds to the Lewis base site of Al₂O₃, while a proton is abstracted from the –B(OH)₂ group by the Brønsted base surface site of Al₂O₃ (**Figure 5.5**, step I-II). Meanwhile, Ru(bpy)₃²⁺ is photoexcited by the 7 W LED lamp to produce Ru(bpy)₃^{2+*}, which donates a single electron to adsorbed O₂ to form Ru(bpy)₃³⁺ and superoxide (step II-III), which would accept protons abstracted by

the Brønsted base surface sites of Al₂O₃ as well as the hydrocarbon groups of neighbouring boronic acid molecules (**Figure 5.5**, step III-IV). Single electron transfer from the boronic acid surface complex to Ru(bpy)₃³⁺ and the subsequent cleavage of the O-O bond would then release phenol (**Figure 5.5**, step IV-V). At the same time, three neighbouring boronic acid groups, having lost a proton, a hydrocarbon group and two electrons each, would bind together to form metaboric acid (**Figure 5.5**, step V-I). In this way, the Al₂O₃-Ru(bpy)₃²⁺ dual surface complex system would have enabled the overall transfer of two hydrocarbon groups, four electrons and two protons from two boronic acid molecules to an adsorbed oxygen molecule.

Figure 5.5 Proposed mechanism of visible-light-driven phenylboronic acid oxidation by the Al₂O₃ and Ru(bpy)₃²⁺ surface complex system.

5.3.4 Conclusion

In conclusion, we have successfully demonstrated that the Brønsted base surface properties of metal oxides can be utilized for selective photocatalytic organic transformations. The MO_x-Ru(bpy)₃²⁺ dual surface complex system enabled high yields of alcohols from boronic acids, even though MO_x nor Ru(bpy)₃²⁺ individually could only induce low yields of alcohols. The proximity of the Brønsted base sites appear to be crucial towards the reaction, which suggests that the reaction mechanism involves the interaction of two or more boronic acids with O₂. The strength of the Brønsted base sites appear to be another factor influencing the reaction; there seems to be a positive relationship between the yields of alcohol and the quantity of strong Brønsted base sites of Al₂O₃, rather than with the quantity of weak or all Brønsted base sites. The reaction proceeds via a photocatalytic aerobic pathway, and can work with a plethora of photosensitizers of different moieties. This discovery highlights a significant role that heterogeneous surfaces may play in contributing to photocatalytic organic transformations, thus opening up the possibility of utilizing surface complexation mechanisms between the reactants and earth-abundant materials to bring forth a wider range of photoredox transformations. Such benign and environmentally green organic transformations that utilize sustainable and abundant resources such as sunlight and Al₂O₃ are potentially beneficial to industrial conversion of raw materials into valuable products, such as in the pharmaceutical, flavor and fragrance industries.

Chapter 6

Carbon-Doped Al₂O₃ for Photocatalytic Organic Transformations of Benzylamines to Imines

In the previous chapters, Al₂O₃ surface complexation was used to enable photocatalytic organic transformations. The photocatalytic reaction was initiated by the visible light induced electron-hole separation of the dye photosensitizer, while Al₂O₃ served to provide Brønsted base sites, or to reduce the oxidation potential of the reactant, benzylalcohol, as well as enable electron transfer from the photo-excited dye to chemisorbed molecular O₂. To further simplify this system, it is theorized that Al₂O₃ and the photosensitizer can possibly be combined into a single heterogeneous catalyst through carbon-modification. This would enable Al₂O₃ to absorb visible light and form electron-hole pairs without the aid of a dye. The resultant carbon-modified Al₂O₃ (C-Al₂O₃) can realize the selective oxidation of benzylamines to imines under visible light. Imines are important precursors of industrial production, especially in pharmaceuticals and agrochemicals.⁴¹ The selective photocatalytic aerobic oxidation of amines is a desirable route for the synthesis of imines as it is relatively safe and driven by two naturally-occurring and abundant resources: sunlight and oxygen.

Leow, W. R.; Zhang, Y.; Chen, X. D. "Carbon-Doped Al₂O₃ for Dual Photocatalytic Reactions" (Manuscript under preparation)

6.1 Introduction

Previously, we demonstrated the use of Al₂O₃ surface complexation to enable the selective photocatalytic oxidation of benzyl alcohols to benzaldehydes as well as phenylboronic acids to phenols. In the aforementioned system, the photocatalytic reaction was initiated by the visible light induced electron-hole separation of the dye photosensitizer, while Al₂O₃ either served to reduce the redox potential of the reactant, i.e., benzylalcohol and O₂, or facilitate the proton transfer between reactants, i.e. phenylboronic acids and O₂. To further simplify this system, we theorized that Al₂O₃ and the photosensitizer can possibly be combined into a single heterogeneous catalyst by modification of Al₂O₃. This would enable Al₂O₃ to absorb visible light and form electron-hole pairs without the aid of a dye.

Currently, there exists several methods for the modification of wide band semiconductors, such as TiO₂, in order to sensitize them to visible light, such as the introduction of transitional metal dopants such as Cr, Fe and V.¹¹⁸⁻¹²¹ However, this method suffers from thermal instability, atom diffusion, and electron-hole combination at defect sites.¹²² The introduction of non-metallic elements such as B, N, C or S has been proven superior in this regard.^{118,123,124} In particular, the introduction of carbon, such as through carbon-doping or the formation of carbon-semiconductor composites, has received particular attention due to ease of fabrication, cheap carbon source and stability.^{123,125,126}

Inspired by the above, we demonstrated the successful sensitization of Al₂O₃ to visible light through modification with carbon. This was achieved through the calcination of Al₂O₃ and glucose mixture, which resulted in the presence of carbon on the Al₂O₃ surface. The carbon-modified Al₂O₃ (C-Al₂O₃) can realize the selective photocatalytic oxidation of benzylamines to imines under visible light. Increasing the amount of carbon generally improves the absorption of visible light and therefore the rate of benzylamine oxidation, up to an optimal carbon amount.

6.2 Experimental Methods

6.2.1 Preparation of Pure and Carbon-Doped Al_2O_3 samples

The $\text{C-Al}_2\text{O}_3$ -n samples were prepared as illustrated in **Figure 6.1a**. Firstly, 7.5 g of aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and varying quantities of glucose ('n' = 2, 5, 10, 30 g) were dissolved in deionized water. The pH of the mixtures were then adjusted to 7.0 by the addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution, upon which the formation of white $\text{Al}(\text{OH})_3$ sol-gels could be observed. The sol-gels were allowed to age with stirring for 12 h before being subjected to drying at 90°C . Finally, the dried sol-gels were annealed at 600°C for 6 h to obtain the $\text{C-Al}_2\text{O}_3$ -n samples. The pure Al_2O_3 sample was synthesized through the same method, except without the addition of glucose (**Figure 6.1b**).

Figure 6.1 Schematic illustration of the synthesis of (a) pure Al_2O_3 and (b) $\text{C-Al}_2\text{O}_3$ -n.

6.2.2 Characterization of the Pure and Carbon-Doped Al₂O₃ samples

The X-ray diffraction (XRD) patterns were obtained on a Bruker-AXS X-ray diffractometer using Cu K_α radiation ($\lambda=1.54178$ Å). The morphologies of the samples were examined by high-resolution transmission electron microscopy (HRTEM, JEOL-JEM-2100F). The Brunauer–Emmett–Teller (BET) surface area was measured with an ASAP 2020 apparatus (Micromeritics Instrument Corp.). UV-visible diffuse reflectance spectroscopy was used to investigate the optical properties of the as-prepared pure and C-Al₂O₃-n samples by a UV-vis spectrophotometer (scan-lambda 750) with barium sulfate as the reference and transformed to the absorption spectra according to the Kubelka-Munk relationship. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD system with a monochromatized Al K α source ($h\nu = 1486.6$ eV). A takeoff angle of 0° relative to the surface normal was used to sample the maximum surface depth. Energy calibration was referenced to the C 1s peak at 284.8 eV.

6.2.3 Evaluation of Photocatalytic Activity

The typical procedure for the oxidation of amines is as follows: The reaction system typically comprises the substrate (0.1 mmol) and catalyst (Al₂O₃-C-n, 25 mg) in the solvent CH₃CN (5 mL) in a 10 mL Pyrex glass bottle. The bottle was sealed with a rubber stopper wrapped with an aluminum crimp cap, and O₂ was introduced through a syringe needle to attain an O₂ pressure of 0.1 MPa. The photocatalytic reactions were carried out with magnetic stirring at room temperature under irradiation by a Xe lamp (300 W, Shimadzu Max 303), equipped with a cutoff filter to filter out light below 300 nm and a broad band filter to remove light above 600 nm. The C-doped Al₂O₃ powder was removed through centrifugation. Using chlorobenzene as the internal standard, the reaction mixture was analyzed by gas chromatograph (GC standard FID detector and a DM-5 amine capillary column (5% polysilarylene, 95% polydimethylsiloxane, 30 m, 0.5 mm $\times$ 0.25 μ m, Dikma) with highly pure N₂ as the carrier gas). The reaction products were determined by comparison of retention times with that of standards.

6.3 Outcome

6.3.1 Characterization of the Pure Al₂O₃ and C-Al₂O₃- n Samples

X-ray diffraction (XRD) analysis confirmed the γ -crystalline nature of both the pure Al₂O₃ and the C-Al₂O₃ samples, as the peaks located at $2\theta = 36.9^\circ$, 45.8° and 67.0° correspond to the (311), (400) and (440) crystal planes of γ -Al₂O₃, respectively (**Figure 6.2a**). HRTEM revealed that C-Al₂O₃ comprised wormhole-like nanostructures with uniform particle size of ca. 7 nm, while pure Al₂O₃ comprised rod-like nanostructures (**Figure 6.2b and c**). This indicates that the glucose works not only as the carbon source, but also as a pore template separating the Al(OH)₃ seeds. Selected area electron diffraction (SAED) revealed that both samples were polycrystalline; two separated diffraction rings corresponding to the (400) and (440) crystal planes could be observed while the rest of the SAED rings are obscure. No appreciable differences in the SAED patterns and HRTEM images were observed between C-Al₂O₃ and pure Al₂O₃.¹²⁷

The optical properties of the C-Al₂O₃ sample with respect to the pure Al₂O₃ sample were subsequently investigated. UV-visible diffuse reflectance spectra of the samples showed that the light absorption of the C-Al₂O₃ extended well into the visible region (380~800 nm) as compared to that of pure Al₂O₃ (**Figure 6.3a**). The photoluminescence spectra of the C-Al₂O₃ sample, when excited at 300 nm, revealed a broad emission peak between 400~500 nm (**Figure 6.3b**). No photoluminescence was observed for the pure Al₂O₃ sample in that wavelength range. It has been reported that porous anodic aluminum oxide (PAAM) fabricated in oxalic acid can generate blue photoluminescence when excited by a lower wavelength light, which was attributed to either oxygen vacancies or oxalic acid impurities. To investigate the origin of violet to blue photoluminescence in C-Al₂O₃, XPS analysis was conducted on both the pure Al₂O₃ and the C-Al₂O₃ samples. XPS spectra normalized to the Al peak showed that the C-Al₂O₃ sample is characterized by a significant increase in the peaks corresponding to C=O, C-O-C and C-C bonds, but not the C-Al bond, which suggests that the

carbonaceous species was formed on the surface of Al₂O₃, rather than doped into the crystal structure (**Figure 6.3c**). The photoluminescence of C-Al₂O₃ may be attributed to these surface carbon species. The EPR spectra appears to support this theory; a signal corresponding to g -value = 2.003 was observed for the C-Al₂O₃ sample but not the pure Al₂O₃ sample, and was similar to the reported value for carbon radicals on Al₂O₃ (**Figure 6.3e**). This indicates that the visible light absorption of C-Al₂O₃ may have originated from the surface carbon species, which would enable electron-hole separation upon irradiation. The electron is then injected to Al₂O₃ surface and, together with the corresponding hole, can be utilized to initiate photoredox transformations (**Figure 6.3f**).

Figure 6.2 a) XRD patterns of the synthesized pure Al₂O₃ and C-Al₂O₃ samples. TEM images of b) pure Al₂O₃ and c) C-Al₂O₃. Inset: SAED image of the pure Al₂O₃ sample.¹²⁷ Reproduced with permission from Reference 127.

Figure 6.3 a) Absorbance spectra and b) photoluminescence spectra of the pure Al_2O_3 and the $\text{C-Al}_2\text{O}_3$ samples. C 1s XPS spectra of c) $\text{C-Al}_2\text{O}_3$ and d) pure Al_2O_3 . e) EPR spectra of the pure Al_2O_3 and the $\text{C-Al}_2\text{O}_3$ samples. f) Scheme of photocatalytic activity in $\text{C-Al}_2\text{O}_3$.

6.3.2 Carbon-Doped Al₂O₃ for the Photocatalytic Oxidation of Benzylamines to Imines under Visible Light

The photocatalytic activity of the visible light sensitive C-Al₂O₃ was demonstrated through the oxidation of benzylamines to imines (**Figure 6.4a**). Using C-Al₂O₃ as a catalyst, high yields of the corresponding imines (25.9–81.3%, with most >75.0%) can be achieved from benzylamines **5a–h** after 20 h with O₂ as the oxidant and 380–600 nm irradiation from a 300 W Xe lamp (**Figure 6.4b**). Poor yield was obtained with **5h** due to the difficulty of the condensation reaction between the acetophenone intermediate and the remaining **5h**.⁴¹ The yield of the imine product for **5g** is nearly half that of **5a**, as the additional phenyl group on **5g** imposes steric hindrance to approaching O₂ molecules or intermediates.⁴¹ It should be noted that only low yields (5.7–51.7%, with most <10.0%) were achieved with pure Al₂O₃. The photocatalytic aerobic pathway was confirmed by the negligible yield of imine in the dark and under nitrogen atmosphere (**Figure 6.4c**).

Figure 6.4 a) Visible light driven oxidation of benzylamine to imine with molecular O₂. b) The generality of reaction towards different benzylamine derivatives. d) The importance of light and O₂.

6.3.3 Proposed Mechanism

The proposed mechanism for the selective photocatalytic oxidation of amines under visible light and molecular O₂ is shown as follows. The N atom of **5a** is a Lewis base and thus binds to a Lewis acid site on the Al₂O₃ surface (**Figure 6.5**, step I-II). The surface carbon on Al₂O₃ undergoes electron-hole separation under visible light illumination. O₂ molecule adsorbed on the Al₂O₃ surface would accept the free electron (see **Section 4.3.5**), while the adsorbed **5a** would lose an electron to the surface carbon and undergo C-H dissociation, resulting in the formation of superoxide and carbocation radical, respectively (**Figure 6.5**, step II-III). The superoxide would then form an O₂ bridge with the carbocation radical (**Figure 6.5**, step IV). Synchronous cleavage of C-N and O-O would release a benzaldehyde intermediate, which is susceptible to nucleophilic attack by another unreacted **5a** molecule to form imine **6a** (**Figure 6.5**, step V).

Figure 6.5 Proposed mechanism of photocatalytic benzylamine oxidation by C-Al₂O₃.

6.3.4 Variation of Carbon Content in C-Al₂O₃

The amount of carbon on the Al₂O₃ surface can be easily tuned by adjusting the amount of glucose precursor used during its synthesis. The XRD and UV-visible diffuse reflectance spectra (DRS) of the C-Al₂O₃-n samples are shown in **Figure 6.6a-c**. It can be seen that all of the C-Al₂O₃-n samples are of the γ -crystalline phase (**Figure 6.6a**), but the extent of visible light absorption increases with increasing glucose amount, with the downward slope of the absorbance peak approaching linearity from 300~800 nm (**Figure 6.6b**). This is reflected by the color of the samples, which ranges from the white of pure Al₂O₃, to varying shades of yellow as the carbon content increases, and finally to dark brown in C-Al₂O₃-30 (**Figure 6.6c**). The yield of the reaction was measured at every 4 h for each of the C-Al₂O₃-n samples and plotted against time (**Figure 6.6d**). The rate of reaction generally increases with increasing carbon content, up until C-Al₂O₃-10, after which it decreases, thus indicating that C-Al₂O₃-10 is the best catalyst out of these samples. The increase in reaction rate may be attributed to the increase in visible light utilization with increasing carbon content (**Figure 6.6b**). The subsequently decrease in photocatalytic ability may be due to a reduction in Al₂O₃ surface available for catalysis due to oversaturation of carbon. The photocatalytic ability of C-Al₂O₃-n may be due to the interplay of several factors, including visible light absorption and surface chemistry, and the outstanding photocatalytic performance of C-Al₂O₃-10 may mean that it has achieved the optimal balance among these properties.

Figure 6.6 a) XRD patterns of the synthesized C- Al_2O_3 -n samples. b) UV-visible diffuse reflectance spectra of the synthesized C- Al_2O_3 -n samples. c) Photographs of the synthesized samples. From the left: pure Al_2O_3 , C- Al_2O_3 -2, C- Al_2O_3 -5, C- Al_2O_3 -10, C- Al_2O_3 -30. d) Reaction profiles of benzylamine oxidation on the synthesized C- Al_2O_3 -n samples under visible light irradiation.

6.3.5 Conclusion

This chapter demonstrates the use of a simple and facile solid reaction route to modify the surface of Al₂O₃ with carbon and thus enable its resultant sensitization to visible light. The nature of carbon-modification was elucidated by a series of techniques such as XPS, EPR and photoluminescence. The carbon-modified Al₂O₃ (C-Al₂O₃) can be used for visible light induced photocatalytic organic transformations, as demonstrated by the selective aerobic oxidation of a series of benzylamines to imines. An increase in the carbon content of the C-Al₂O₃ generally leads to an increase in the rate of the photocatalytic transformations, up to an optimal amount, after which the rate decreases. Despite the successful sensitization of Al₂O₃ to visible light, there is still much room for improvement with regards to the photocatalytic efficiency of C-Al₂O₃. Nevertheless, C-Al₂O₃ is still a promising photocatalyst owing to its stability, inexpensive starting materials, and facile synthetic procedure.

Chapter 7

Conclusion and Future Work

In this chapter, the different discussions in this dissertation will be summarized and understood as a comprehensive system. The implications and impact of the findings will be addressed in terms of the extent to which the hypotheses were proven and the degree in which design target was fulfilled. The outstanding questions will also be highlighted, and a discussion will be provided on the opportunities and strategies for future work that can potentially address these questions. Lastly, the predictive power of the original hypotheses towards the outcomes of this dissertation will be examined.

7.1 Summary of Work and Implications/Impact

In this dissertation, we proposed that the surface properties of Al_2O_3 will be able to enable several selective organic transformations in conjunction with a variety of photosensitizers, towards the achievement of high conversions and selectivities. This discovery may subvert our understanding of the role of Al_2O_3 in photocatalytic reactions. It may also bring forth a new methodology of utilizing surface complexation mechanisms between the reactants and earth-abundant materials to effectively achieve a wider range of photoredox reactions.

In the following discussion, we will summarize and analyze our findings with respect to the initial hypotheses.

7.1.1 First Hypothesis: The Redox Potential of the Reactant may be Reduced through Complexation with Alumina to Enable Photocatalytic Organic Transformations

In photocatalytic redox reactions, reaction can proceed only if the redox potential of the photocatalyst is greater than that of the organic reactants²⁰. To achieve this, two strategies are typically used. The first is to compromise visible light absorption through the use of large band gap semiconductors such as TiO_2 and Nb_2O_5 , the second is to increase the redox potential of the photocatalyst through costly and tedious modifications. Here, we have proposed an alternative method to reduce the redox potential of reactants through surface complexation with Al_2O_3 . This is demonstrated through the selective photocatalytic oxidation of benzylalcohols to benzaldehydes. The strong Brønsted base sites on the Al_2O_3 surface abstracts a proton from benzylalcohol to form a benzylalcohol- Al_2O_3 surface complex with reduced oxidation potential, thus rendering it susceptible to oxidation by the photocatalyst. We also made the surprising discovery that the surface complexation of O_2 with Al_2O_3 also activates the adsorbed O_2 for receiving electrons from the photoexcited dyes.

The implication of this study is that the facile addition Al_2O_3 may be used to alter the redox potential of certain reactants when a mismatch occurs between the potentials of the reactant and photocatalyst. We expect that this new methodology of utilizing surface complexation mechanisms between the reactants and earth-abundant materials could possibly achieve a wider range of difficult photoredox organic transformations.

This discovery may subvert our understanding of the role of Al_2O_3 in other photocatalytic reactions. For instance, it may be possible that Al_2O_3 plays a role beyond that of a mere support or scaffold in the performance enhancement in solar hydrogen production⁷⁹ and dye-sensitized solar cells^{114,115}.

7.1.2 Second Hypothesis: The Brønsted and Lewis Acid and Base Sites on the Surface of Metal Oxides can participate as a Co-Catalyst in Photocatalytic Organic Transformations

This hypothesis has been demonstrated by the selective photocatalytic oxidation of phenylboronic acids to phenols. The phenylboronic acid, being a Lewis acid, binds to the Lewis base site of Al_2O_3 . When control experiments are performed with other types of metal oxides, only those with surface Brønsted base sites are able to drive the reaction to completion. Similarly, basic Al_2O_3 produces slightly higher yields of phenols compared to neutral and acidic Al_2O_3 . The addition of acetic acid to quench these Brønsted base sites resulted in dramatically reduced yields of phenols. It is proposed that the surface Brønsted base sites played a crucial role in abstracting protons from the O-H bond of the boronic acid group. The implication of this discovery is that Al_2O_3 can serve as a clean, abundant and environmentally friendly base to mediate proton transfers in organic transformations. It also offers the additional advantages of being stable and easily separable from the reaction for purification of the product.

7.1.3 Third Hypothesis: The Surface Properties of Al_2O_3 and the Photosensitizer can be combined as a Single Heterogeneous Catalyst through Carbon-Modification

Our last hypothesis is that the dye- Al_2O_3 surface complex system can be simplified through the combination of photocatalysis and Al_2O_3 surface catalysis in a single material. This is achieved through the carbon-modification of Al_2O_3 in order to sensitize it to visible light irradiation. The photocatalytic activity of the resultant carbon-modified Al_2O_3 (C- Al_2O_3) was demonstrated through the selective photocatalytic oxidation of benzylamines to imines with high conversions and selectivities.

Having established the photocatalytic activity of C- Al_2O_3 , more work remains in order to understand the mechanism behind its synthesis process, as well as establish its conduction and valence band levels. By establishing the energy levels of C-doped Al_2O_3 and comparing them with the HOMO and LUMO of reactants, we may be able to better understand the mechanism of the organic transformations, as well as predict other possible transformations achievable with the C- Al_2O_3 photocatalyst. It should also be noted that more improvements should be made for C- Al_2O_3 to become an even more effective photocatalyst. For instance, although high conversions and selectivities of benzylamines to imines could be achieved, the reaction time is slow relative to other commonly-used photocatalysts such as TiO_2 . Nevertheless, due to its low cost, stability and environmentally friendliness, C- Al_2O_3 nanomaterials should be promising photocatalysts for selective organic transformations.

7.2 Outstanding Questions

From the aforementioned discoveries, we can see that Al_2O_3 , though paradigmatically known to be an insulator, can be extremely useful in driving photocatalysis. This leads us to wonder if the utility of Al_2O_3 can be extended in other ways, such as the following:

1. Other organic transformations that can similarly be enabled by the Al_2O_3 and dye photocatalytic surface complex system. It would be greatly beneficial to the field of organic chemistry if Al_2O_3 can be used to enable an extremely wide range of organic transformations. Some possibilities include:
 - a. The selective photocatalytic aerobic oxidation of aliphatic alcohols.
 - b. The selective photocatalytic aerobic oxidation of phenolic alcohols.
 - c. The selective photocatalytic aerobic oxidation of other heteroatom organic reactants besides alcohols, such as amines or sulfides
 - d. Photocatalytic organic transformations that utilize the reductive quenching pathway of $\text{Ru}(\text{bpy})_3^{2+}$. In this dissertation, we have mainly utilized the oxidative quenching pathway of $\text{Ru}(\text{bpy})_3^{2+}$. It would be interesting to find out if the Al_2O_3 and dye photocatalytic surface complex system can also be used for the reductive quenching pathway.
 - e. Other types of photocatalytic organic transformations. In this dissertation, we have mainly focused on selective aerobic oxidations. In the future, it would also be meaningful to explore the use of the Al_2O_3 and dye photocatalytic surface complex system to enable other types of organic reactions such as addition reactions or reductive elimination reactions.
2. Other interesting surface properties of Al_2O_3 and the application of these

properties to photocatalytic organic transformations. In this dissertation, we have mainly utilized the strong Brønsted base sites and large areas of the Al_2O_3 surface. However, the Al_2O_3 surface also comprises other interesting sites for with the potential for catalysis, such as Brønsted acid, Lewis acid and Lewis base sites. It would be interesting to find out if these properties can also be used to enable other kinds of photocatalytic organic transformations.

3. Other types of modifications towards Al_2O_3 . In this dissertation, we have studied carbon-modification as a means for the sensitization of Al_2O_3 to visible light. It may be possible to modify Al_2O_3 through other methods, such as N doping or cation doping. Surface modifications may also be considered to enhance or alter certain properties of the Al_2O_3 surface.

7.2.1 Experimental Method for Preliminary Results

All reactants and catalysts were purchased from Sigma Aldrich and used without further purification, and all solvents were purchased from Fisher Chemical. In a typical reaction, 25 mg of Al_2O_3 , 0.5 μmol of $\text{Ru}(\text{bpy})_3\text{Cl}_2$, and 0.1 mmol of $\text{PhB}(\text{OH})_2$ were added to 5 mL of CH_3CN in a Pyrex vessel. O_2 was then purged into the vessel to achieve a pressure of 0.1 MPa. The reaction mixture was then illuminated by the 7 W white light household LED under magnetic stirring at 800 rpm. Upon reaction completion, the Al_2O_3 particles were separated from the reaction mixture by centrifugation. The product identities were confirmed by comparison of the gas chromatography (GC) retention times with that of standard samples. The products were then quantitatively analyzed through a GC (Agilent 7890A) equipped with a flame ionization detector (FID) and Agilent Technology 19091J-413 capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 mm) using high-purity N_2 as the carrier gas and chlorobenzene as the internal standard. The standard analysis conditions are: injector temperature 250 $^\circ\text{C}$, detector temperature 300 $^\circ\text{C}$, column temperature ramped from 50 $^\circ\text{C}$ to 300 $^\circ\text{C}$ with a rate of 20 $^\circ\text{C min}^{-1}$.

7.2.2 Al₂O₃ and Dye Surface Complex System for Photocatalytic Organic Transformation of Aliphatic Alcohols to Aldehydes

Besides aromatic alcohols, we propose that the Al₂O₃ and dye photocatalytic surface complex system can possibly be used to selectively oxidize aliphatic alcohols to aldehydes (**Figure 7.1**). We have attempted some preliminary tests with 1-butanol **7a**, 1-pentanol **7b**, and cyclohexanol **7c**. The results show that the addition of Al₂O₃ can lead to a slight increase in the yield compared to that of the unassisted dye (**Table 7.1**). However, the yield is still quite low. More work may have to be done in order to improve the catalytic activity of the Al₂O₃ and dye photocatalytic surface complex system towards the yield of aliphatic aldehydes.

Figure 7.1 Selective photocatalytic oxidation of aliphatic alcohols.

Table 7.1 Yields of aldehydes from the selective photocatalytic oxidation of aliphatic alcohols. Catalyst: [a] 0.5 μmol Ru(bpy)₃Cl₂, [b] 0.5 μmol Ru(bpy)₃Cl₂ and 50 mg Al₂O₃.

Entry	Substrate	Product	Yield [%] ^[a]	Yield [%] ^[b]
1	7a	8a	0.205	8.42
2	7b	8b	0.243	6.70
3	7c	8c	0.130	4.88

7.2.3 Al₂O₃ and Dye Surface Complex System for Photocatalytic Organic Transformation of Phenols

Having successfully demonstrated the oxidation of benzylic C-O bonds, another outstanding question from this dissertation is whether phenylic C-O bonds can be similarly oxidized with the Al₂O₃ and dye photocatalytic surface complex system. To this end, we have conducted some preliminary experiments on the selective photocatalytic oxidation of phenol **9a** and hydroquinone **9b** to benzoquinone **10a** (**Figure 7.2**). The results show that the addition of Al₂O₃ can significantly enhance the rate of the reaction compared to that of the unassisted dye (**Table 7.2**). More work will need to be done to understand the mechanism of the reaction, as well as the extensiveness of the system towards different phenols.

Figure 7.2 Selective photocatalytic oxidation of aliphatic phenols.

Table 7.2 Selective photocatalytic oxidation of phenols. Catalyst: [a] 0.5 μmol Ru(bpy)₃Cl₂, [b] 0.5 μmol Ru(bpy)₃Cl₂ and 50 mg Al₂O₃.

Entry	Substrate	Product	Yield [%] ^[a]	Yield [%] ^[b]
1	<chem>Oc1ccccc1</chem> 9a	<chem>O=C1C=CC(=O)C=C1</chem> 10a	0	14.5
2	<chem>Oc1ccc(O)cc1</chem> 9b	<chem>O=C1C=CC(=O)C=C1</chem> 10b	21.0	61.3

7.2.4 Al_2O_3 as a carrier platform for insoluble dyes

Besides alcohols, we also wondered if the Al_2O_3 and dye photocatalytic surface complex system can be used for other heteroatom organic reactants, such as amines or sulfides. The preliminary data shows that although benzylamine **5a** can be easily oxidized by $\text{Ru}(\text{bpy})_3^{2+}$ alone. However, $\text{Ru}(\text{dcbpy})_2(\text{bpy})^{2+}$, being insoluble in the solvent CH_3CN , is unable to oxidize benzylamine (**Figure 7.3**). This can be easily resolved by anchoring $\text{Ru}(\text{dcbpy})_2(\text{bpy})^{2+}$ on the surface of Al_2O_3 , which allows the insoluble dye access to the reactant.

Figure 7.3 Photocatalytic aerobic oxidation of benzylamine to imine with $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{dcbpy})_2(\text{bpy})^{2+}$, and $\text{Ru}(\text{dcbpy})_2(\text{bpy})^{2+}$ with Al_2O_3 .

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List of Publications

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2. Leow, W. R.; Chen, X. D.* "Al₂O₃ Surface Complexation for Photocatalytic Organic Transformations for Phenylboronic Acids to Phenols" (**Manuscript under preparation**)
3. Leow, W. R.; Zhang, Y.; Chen, X. D.* "Carbon-Doped Al₂O₃ for Dual Photocatalytic Reactions" (**Manuscript under preparation**)
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