Studies on Selective Organic Transformations by Semiconductor Photocatalysts Loaded with Platinum and Palladium Nanoparticles

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Abstract

There has been much interest in the development of environmentally- and economically-friendly chemical processes for organic synthesis from the viewpoint of green and sustainable chemistry. The main objective of this thesis is to develop the photocatalytic processes for selective organic transformations. Semiconductor metal oxides loaded with platinum (Pt) and palladium (Pd) nanoparticles were used for photocatalytic transformations under UV and visible light irradiations. This thesis consists of following six chapters.

In Chapter I, photocatalytic synthesis of benzimidazoles from alcohols and  o-arylenediamines was studied using titanium dioxide loaded with Pt nanoparticles (Pt/TiO₂) under UV irradiation. The catalytic system efficiently produces benzimidazoles with high selectivity. Experimental results reveal that the reaction is achieved by Pt-assisted photocatalytic oxidation of alcohols to aldehydes on the TiO₂ surface, followed by dehydrogenation of benzimidazoline intermediate on the Pt surface. Amount and size of Pt particles play crucial roles on reaction. The catalyst loaded with 0.2 wt% Pt, which contains 2.0 nm Pt particles, exhibits the highest activity and selectivity.

In Chapter II, TiO₂ loaded with Pd nanoparticles (Pd/TiO₂) were used for photocatalytic hydrodenitrogenation of aromatic cyanides with ethanol as a hydrogen source under UV irradiation. The catalyst promotes selective hydrodenitrogenation of aromatic cyanides, and produces corresponding toluene derivatives and triethylamine with almost quantitative yields. Experimental evidences and model calculation revealed that the catalytic activity strongly depends on the amount of Pd loaded. The catalyst containing 2 wt% Pd, with a relatively low Schottky barrier height at the Pd-TiO₂ heterojunction and a large number of surface Pd atoms, exhibits the highest denitrogenation activity.

In Chapter III, the Pd/TiO₂ catalysts were used for N-monooalkylation of primary amine with alcohol under UV irradiation. The catalyst efficiently promotes the corresponding secondary amine with almost quantitative yields. The reaction occurs via tandem photocatalytic and catalytic reactions, consisting of Pd-assisted photocatalytic alcohol oxidation to produce aldehyde, catalytic condensation of aldehydes with amines, and catalytic hydrogenation of formed imines with the hydrogen atom formed on the Pd particles (H-Pd species). Experimental evidences and model calculation reveal that the rate-determining step is the imine hydrogenation, and the reaction depends strongly on the size of Pd particles. The catalyst with 0.3 wt% Pd, containing 2-2.5 nm Pd particles, shows the highest activity for imine hydrogenation, and smaller or larger Pd particles are inefficient.

In Chapter IV, TiO₂ loaded with bimetallic Pd-Pt alloy nanoparticles were used for photocatalytic dehalogenation of aromatic halides with alcohol as a hydrogen source under UV irradiation. The alloy catalytic system efficiently promotes dehalogenation, and the activity is three times higher than that of the catalyst loaded with Pd alone and is also higher than that obtained with molecular hydrogen as a hydrogen source. The high catalytic activity of the alloy catalyst is due to the enhanced consumption of photoformed
electrons on the Pt site and the efficient transfer of the formed hydrogen atom to the adjacent Pd site within the alloy particles, leading to efficient formation of the hydride species, which act as the active species for dehalogenation.

In Chapter V, tungsten trioxide (WO₃) loaded with Pt nanoparticles (Pd/WO₃) were used for partial oxidation of cyclohexane (CHA) with molecular oxygen (O₂) under visible light irradiation (λ > 420 nm). The Pt/WO₃ catalysts produce cyclohexanol (CHA-ol) and cyclohexanone (CHA-one) with high selectivity (ca. 93%). The high selectivity for partial oxidation on Pt/WO₃ is because subsequent decomposition of CHA-ol and CHA-one is suppressed. In the Pt/WO₃ system, the photoformed electrons on the conduction band of WO₃ are efficiently consumed by a multi-electron reduction of O₂ (formation of water and hydrogen peroxide), where a single-electron reduction of O₂ is unfavorable. This suppresses the formation of a superoxide anion that promotes decomposition of CHA-ol and CHA-one and, hence, results in selective formation of partial oxidation products.

In chapter VI, Pt particles loaded on anatase TiO₂ (Pt/anatase) were used for aerobic oxidation of alcohols under visible light irradiation (λ > 450 nm). The reaction is initiated by the absorption of visible region light by Pt nanoparticles. This promotes interband excitation of d electrons on Pt nanoparticles. This then leads to smooth electron transfer to anatase and promotes the reduction of O₂ on anatase. Model calculation with Pt nanoparticles also reveals that this activity depends on the height of Schottky barrier and the number of perimeter Pt atoms created at the Pt/anatase heterojunction. The catalyst loaded with 2 wt% Pt, containing 3–4 nm Pt particles, facilitates smooth Pt→anatase electron transfer, resulting in the highest photocatalytic activity. The catalyst also promotes efficient and selective aerobic oxidation of alcohols by sunlight exposure.

This thesis described the selective organic transformations by semiconductor photocatalysts loaded with Pt and/or Pd nanoparticles. These results presented in this thesis may contribute to the development of selective photocatalytic organic transformations and the design of more environmentally- and economically-friendly synthesis processes by sunlight.
Preface

This dissertation work was carried out under the joint supervision of Professor Dr. Takayuki Hirai and Associate Professor Dr. Yasuhiro Shiraishi at the Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University from 2007 to 2013.

The objective of this thesis is the design and development of selective systems for photocatalytic organic transformations by semiconductor metal oxides loaded with platinum and palladium nanoparticles. The author hopes that the results obtained in this work would give some suggestions for the future construction of photocatalytic systems for organic synthesis.

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ENERGY and ENVIRONMENT are two of the humanity’s top ten problems for next 50 years. Since the industrial revolution in 18th century, human beings used large amount of resources and energies, and built up enough material civilization, leading to obtaining an easy and comfortable life. The human beings who are one of the species on the earth, however, have caused a crisis of biogeocenosis of the earth. The origin of this disaster is not only the development and expansion of industry based on technologies but our lifestyle which have grown dramatically since the industrial revolution. Increase of energy consumption, world population, and food consumption, gave rise to the global disasters such as warming temperature, acid rains, and ozone depletion. Therefore, businesses, governments, and consumers shall cooperate for taking measures against the protection of earth resources and environment. Chemical industry, which is one of the various industries, produces various chemical precursors of automobiles, constructs, clothes, and drugs to other industries and has an important part in our lifestyle. Chemical industry, therefore, has the potential to contribute to environmental protection of the earth by reviewing lifecycle (from production to disposal) of chemical products.

One of the solutions by approaching from the chemical industry is the introduction of the concept of “Green chemistry”. This concept means “the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances,” which is a comprehensive approach applicable to all aspects of chemistry. From feed stocks to solvents, synthesis, and process, green chemistry actively seeks ways to produce materials which are more benign to human health and the environment. The current attention on green chemistry reflects a shift away from the historic “command and control” approach to environmental problems that restrictive waste treatment and control and clean up through regulation, and toward preventing pollution at its source. Therefore, rather than accepting waste production and disposal as unavoidable, green chemistry seeks new technologies that are cleaner and economically competitive.

The economic benefits of green chemistry are central locomotives in its advancement. Industry is also able to adopt green chemistry methodologies because they improve the corporate bottom line; a wide variety of operating costs is decreased through the use of green chemistry. When less waste is generated, environmental compliance costs go down, leading to the decrease of needs of treatment and disposal. Decreased solvent usage and fewer processing steps lessen the material and energy costs of manufacturing and increase material efficiency. The environment, human health, and the economic
advantages realized through green chemistry are, therefore, serving as a strong incentive to industry to adopt greener technologies.

Developing the green chemistry methodologies is a challenge that may be viewed through the framework of “Twelve Principles of Green Chemistry”. These principles identify CATALYSIS as one of the most important tools for implementing green chemistry. In addition, even from the chemical industry, an improvement of catalysis process, which is one of the main and fundamental parts of manufacturing process, hold the promise of reduction of produce costs. The design and application of new catalysts and catalytic systems, therefore, offer numerous green chemistry benefits including lower energy requirements, catalytic versus stoichiometric amounts of materials, increased selectivity, and decreased use of processing and separation agents. These also allow the use of less toxic materials, which leads to achieving the dual goals of environmental protection and economic benefit simultaneously. Especially, heterogeneous catalysis has received a tremendous amount of interest, both from a scientific and an industrial perspective. This is demonstrated by the 2007 Nobel Prize in Chemistry awarded to Prof. Ertl, a pioneer in introducing surface science techniques to the field of heterogeneous catalysis leading to a deeper understanding of how chemical reactions take place at surfaces. Since more than 90% of chemical manufacturing processes utilize catalysts, heterogeneous catalysis has an enormous impact on the world economy. The current manufacturing processes, however, have taken large energy to purify the chemical products and precursors due to the low yields of catalytic reaction products. These processes also need severe reaction conditions (high temperature and high pressure) to increase the yields per unit time, although sub-reactions proceed and specific reactors are required. For the improvement of these processes, catalytic productions of an only main product under more economically and environmentally benign conditions are desirable.

Metal nanoparticle catalysis is one of the most attracted fields in heterogeneous catalysis. Several remarkable novel catalytic properties including enhanced reactivity and selectivity have been reported for nanoparticle catalysts as compared to their bulk counterparts. To utilize the power of these nanoparticle catalysts, detailed understanding of the origin of their enhanced performance is necessary. Many experimental studies on nanoparticles have focused on correlating catalytic activity with particles size. While particle size is an important consideration, many other factors such as geometry, composition, oxidation state, and chemical/physical environment can also play an important role in determining nanoparticle reactivity. The exact relationship between these parameters and the catalytic performance may, however, be system dependent. A systematic understanding of the factors that control catalyst reactivity and selectivity is therefore very important task.
Metal nanoparticles are often used in the field of photocatalysis. Photocatalytic reaction is a recent discipline particularly well adapted to environmental problems since it operates at room temperature by catalytic photoactivation instead of thermal activation. Among them, titanium dioxide (TiO₂) has been widely used as a pigment in sunscreens, paints, ointments, or toothpaste, because it is chemically stable, harmless, and inexpensive. In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes.⁶ As a result of this, the application of TiO₂ photocatalysis was extended to environmental frontiers. Frank and Bard⁷ reported the application of TiO₂ in photocatalytic oxidation of CN⁻ and SO₃²⁻ in aqueous medium under sunlight irradiation. Photocatalytic reduction of CO₂ on TiO₂ reported by Inoue et al.⁸ have attracted much attention in this field. Moreover, Izumli et al.⁹ have reported that photo-kolbe decarboxylation route to butane, which includes the generation of hydroxyl radical. This opened a new chapter for application of TiO₂ photocatalysis in organic transformations. Kraeutler and Bard.¹⁰ have applied the decomposition of organic compounds by TiO₂ photocatalysis.

The mechanism for heterogeneous photocatalysis has been studied extensively so far, and a number of excellent reviews and books have been published by many researchers.¹¹ Despite many applications, the basic mechanisms are almost similar. Figure 1 shows schematic representation of the photocatalytic reaction on TiO₂. When TiO₂ absorb light with energy larger than its bandgap energy (Eₘ), photoexcited electron (e⁻) and holes (h⁺) pairs are generated in the conduction band and valence band, respectively. The e⁻ and h⁺ produced inside the particles migrates to the particle surface and promotes oxidation and reduction reactions, while some of these pairs are deactivated by recombination of them at bulk or surface. In the presence of molecular oxygen (O₂), the reduction of O₂ by conduction band e⁻ proceeds.
In contrast, the $h^+$ oxidizes substrates or $H_2O$.

In 2000s, the growing awareness of green chemistry has given a boost to develop the process for organic synthesis with photocatalysts under mild conditions, which avoid stoichiometric consumption of expensive and harmful oxidants. Wide application of TiO$_2$ photocatalysis for organic transformations has been reported. Some of the transformations were accomplished, which can be categorized as oxidations and oxidative cleavages, reductions, geometric and valence isomerizations, substitutions, condensations, and polymerizations. However, except for above some successful examples, photocatalytic organic transformations on TiO$_2$ basically do not proceed efficiently.

One of the reasons for unsuccessful organic transformations on bare TiO$_2$ is the low activity for photocatalytic reactions. As shown in Figure 1, photoexcited semiconductor materials produce $e^-$ and $h^+$. They migrate thorough the material and appear on the surface, promoting oxidation and reduction reactions of substrates. The parts of $e^-$ and $h^+$ are, however, recombined during migration and are deactivated. To improve the activity for photocatalysis, therefore, it is necessary to suppress the charge recombination between photogenerated $e^-$ and $h^+$ (Figure 2a). One of the most famous methods to solve this problem is the surface modification of photocatalysts with noble metal nanoparticles such as Pt, Ag, Au, and Pd. Among them, modification of TiO$_2$ surface with Pt nanoparticles (Pt/TiO$_2$) is a popular method, which was firstly reported by Kraeutler and Bard. The Pt/TiO$_2$ catalyst exhibits enhanced activity for various photocatalytic reactions. This is basically due to their different Fermi levels ($E_F$), characterized by the work function of the metals and the band structure of the semiconductors. When metal nanoparticles are loaded on the semiconductor surface, the electrons migrate from semiconductor to metal occurs until the two Fermi levels are aligned similar, and energy barrier is created at the interface of heterojunction, which is called the Schottky barrier (Figure 2b). Photoexcitation of semiconductor generates electrons in the conduction band of the semiconductor and raises its Fermi level to more negative values. Then, the generated energetic difference at the semiconductor and metal interface drives the electrons from the conduction band of the semiconductor into the metal nanoparticle. The Schottky barrier produced at the metal-semiconductor interface can serve as an efficient electron trap preventing electron-hole recombination in photocatalysis, which leads to the enhancement of photocatalytic reactivity. The activity of these photocatalyst is usually tested by degradation of organic pollutants in water or photocatalytic $H_2$ evolution from aqueous alcohols solutions under UV light irradiation. Application of these modified TiO$_2$ photocatalysts for photochemical organic transformation is scarce.
Figure 2. Schematic representation for (a) the photocatalyst with/without metal nanoparticles and (b) the Schottky barrier created at the metal and semiconductor photocatalyst heterojunction.

As mentioned before, in the last century, catalysis developed into one of the most powerful technologies in the petroleum, bulk chemical, fine chemical and pharmaceutical industries. In parallel to developing technologies, the fundamental understanding of catalytic processes has been advancing rapidly by developing model catalytic system using experimental and theoretical techniques at the molecular level. In particular, noble metal nanoparticle catalysts possess marvelous and specific activities about various reactions. The pioneering catalytic applications of noble metal nanoparticles were reported in 1940 by Nord and co-workers for nitrobenzene reduction. In the late 1950s, Boreskov stated a chemical approach to the kinetics of heterogeneous catalysis by metals based on the influence of the reaction mixture and reaction conditions on the properties and chemical composition of the catalyst. Since the 1970s, metal nanoparticles have been more frequently used in catalysis, and are even suspected to be involved in organometallic catalysis. Since the turn of the millennium, interest in
metal nanoparticle catalysis has considerably increased because this class of catalysts appears as one of the most promising solutions toward efficient reaction under mild, environmentally benign conditions in the context of Green Chemistry.\textsuperscript{30} As present, these preparation, structure determination, and applications are topics of current interest.\textsuperscript{31} Especially, attention is focused on that a change in the catalytic properties of metals, caused by the transformation from bulk metal to nanoparticles (1-100 nm), is one of the fundamental problems of heterogeneous catalysis.\textsuperscript{32} Supported metal particle size can also essentially affect the specific catalytic activity (reaction rate per one surface atom), the number of reaction cycles, as well as the rate of the catalytic reaction. As suggested,\textsuperscript{33} these changes may be associated both with the electronic properties of nanoparticles and with features of their crystal structure (compared with bulk metal or coarse particles, the most part of surface atoms with low coordination numbers and with residing at the angles and edges of fine particles).

Among metal nanoparticles, platinum (Pt) and palladium (Pd), which are well known as platinum group metals, possess dominantly specific and various catalytic activities. Extensive studies for Pt and Pd nanoparticles have been performed for various catalytic applications. Pt nanoparticles show outstanding catalytic and electrical properties and superior resistant characteristics to corrosion, and have been widely applied in chemical, petrochemical, pharmaceutical, electronic, and automotive industries.\textsuperscript{34} They possess distinctive ability in catalyzing partial oxidation, hydrogenation and dehydrogenation of a variety of important molecules that are essential in many industrial processes.\textsuperscript{35} In contrast, Pd nanoparticles are well known as noble metal catalysts which possess the high activity for various reactions.\textsuperscript{36} The main parts of these reactions by Pd nanoparticles are hydrogenations and C-C couplings (Suzuki, Heck, Stille),\textsuperscript{37} and a few reports are related to other processes like dehalogenation, hydrodechlorination, carbonylation or oxidation.

In addition, bimetallic nanoparticles, composed of two different metal elements, are of greater interest than monometallic ones, from both the scientific and technological views, for the improvement of the catalytic properties of metal nanoparticles.\textsuperscript{38} In fact, bimetallic catalysts have long been valuable for in-depth investigations of the relationship between catalytic activity and catalyst particle structure.\textsuperscript{39} This is because bimetallization can improve catalytic properties of the original monometallic catalysts and create a new property, which may not be achieved by monometallic catalysts. These effects of the added metal component can often be explained in terms of an ensemble and/or a ligand effect in catalyses. Sinfelt et al. have made a series of studies on bimetallic nanoparticle catalysts supported on inorganic supports, for example Ru-Cu\textsuperscript{40} and Pt-Ir\textsuperscript{41} on silica. They analyzed the detailed structures of their samples by an extended X-ray absorption fine structure (EXAFS) technique, and showed that these
nanoparticles with a diameter of 1-3 nm had an alloy structure, associated with their properties.\textsuperscript{42}

\textbf{Photocatalysis} \hspace{2cm} \textbf{Catalysis}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.png}
\caption{Schematic representation for the concept of selective photocatalytic and catalytic organic transformations by photocatalyst loaded with noble metal nanoparticles.}
\end{figure}

On the basis of these findings, if photocatalyst and noble metal nanoparticles are combined, some new photocatalytic reactions for selective organic transformation under mild reaction conditions are prospective (Figure 3). TiO\textsubscript{2} is an efficient photocatalyst under UV irradiation. It has wide band-gap (3.0–3.2 eV), which almost corresponds to an absorption threshold of ca. 400 nm. This limits the use in the visible wavelength region (400–800 nm). It is well known that <400 nm UV light is contained in solar radiation with only 3–5\%. This means that only a small portion of light can be used for chemical reactions. Development of photocatalysts that work under visible light irradiation is an important issue for practical application of “sunlight” as the light source. One approach is the use of semiconductor photocatalysts with narrow band gap (<3.0 eV). Warrier et al. reported that CdS and CdSe quantum dots in the presence of sacrificial electron donors promote chemoselective photocatalytic reduction of aromatic azides to aromatic amines.\textsuperscript{43} Ohmori et al. reported that α-Fe\textsubscript{2}O\textsubscript{3} is capable of oxidizing water and evolving oxygen gas, in the presence of Fe\textsuperscript{3+} as the electron scavengers.\textsuperscript{44} Tungsten trioxide (WO\textsubscript{3}) is also a visible-light-responsive photocatalyst, which possesses narrow band gap (2.8 eV), deep oxidation potential of valence band, nontoxicity, and stability (Figure 4).\textsuperscript{45} Abe et al. have proposed that Pt loading is an attractive solution to enhance the photocatalytic properties because loaded Pt enable to trap photogenerated electron from WO\textsubscript{3} to reduce O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O.\textsuperscript{46} Arai et al. reported that WO\textsubscript{3} loaded with Pd catalyst proceed complete oxidation of acetaldehyde and toluene under visible light irradiation.\textsuperscript{47}
The redox potential of TiO$_2$ and WO$_3$ is shown in Figure 4. The other approach is the use of localized surface plasmon resonance (SPR) of a portion of noble metal nanoparticles. In 2004, Tian et al. found that Au or Ag particles loaded on a semiconductor TiO$_2$ film that is coated on an indium tin oxide electrode generates an anodic photocurrent in the presence of Fe$^{2+}$ under visible light irradiation ($\lambda > 420$ nm) (Figure 5). This photoelectrochemical response is explained by an electron transfer mechanism similar to that for dye-sensitized TiO$_2$: collective oscillations of electrons on the Au particles irradiated by the incident light transfers the electrons from the Au particles to the TiO$_2$ conduction band, while the positively charged Au particles receive electrons from the electron donor (Fe$^{2+}$). On the basis of these findings, they proposed that semiconductor materials loaded with a portion of noble metal nanoparticles behaves as a new class of visible light-driven catalysts. Since then, effects of preparation procedure, metal particle sizes, loading amount, and on photocatalytic activity has been investigated for photodegradation of organic substrates, and $\text{H}_2$ and $\text{O}_2$ evolution from water. Application to organic transformations has scarcely been carried out.

The purpose of this thesis is to develop selective organic transformations by semiconductor photocatalysts loaded with Pt and Pd nanoparticles. The author tried to apply the TiO$_2$-based photocatalysts loaded with Pd and Pd nanoparticles for benzimidazole synthesis, hydrodenitrogenation of aromatic cyanide, and N-alkylation of primary amines under UV irradiation. Moreover, the author used the synergetic effect promoted by bimetallic Pt-Pd alloy nanoparticles for selective hydrodehalogenation of organic halides. To create the photocatalytic system driven by visible light irradiation, the author used WO$_3$ catalysts loaded with Pt nanoparticles for partial oxidation of CHA. In addition, the author tried to clarify the visible light activity of Pt nanoparticles loaded on TiO$_2$ surface.
and clarified the potential for sunlight-driven organic transformations. The framework of the present study is shown in Figure 6.

**Figure 5.** TiO$_2$-loaded with Au metal nanoparticles showing surface plasmon resonance.
Photocatalytic Activation by UV Light

Chapter I.
Synthesis of Benzimidazoles on TiO₂ Loaded with Pt Nanoparticles

Chapter II.
Hydrodenitrogenation of Aromatic Cyanides on TiO₂ Loaded with Pd Nanoparticles

Chapter III.
N-Monoalkylation of Amines with Alcohols on TiO₂ Loaded with Pd Nanoparticles

Chapter IV.
Dehalogenation of Organic Halides on TiO₂ Loaded with Bimetallic Pd-Pt Alloy Nanoparticles

Photocatalytic Activation by Visible Light

Chapter V.
Partial Oxidation of Cyclohexane on WO₃ Loaded with Pt Nanoparticles under Visible Light Irradiation

Chapter VI.
Aerobic Oxidation by Platinum Nanoparticle Supported on Anatase Titanium Dioxide under Visible Light Irradiation

Figure 6. Framework of the present study.
This thesis consists of six chapters. The first four chapters (Chapters I–IV) describe photocatalytic organic transformations under UV irradiation, where TiO₂ loaded with Pt or Pd nanoparticles and TiO₂ loaded with Pd–Pt bimetallic alloy nanoparticles were employed. The chapters V and VI describe visible light-driven photocatalysts, where WO₃ loaded Pt nanoparticles and TiO₂ loaded with Pt nanoparticles are used for selective organic transformations.

In Chapter I, TiO₂ particles loaded with Pt nanoparticle (Pt/TiO₂), prepared by photodeposition method, was used for one-pot catalytic synthesis of benzimidazole from o-phenylenediamines and alcohols. We found that the process successfully produces corresponding benzimidazoles rapidly and selectively. This process is promoted by Pt-assisted photocatalytic oxidation of alcohols to aldehydes and catalytic dehydrogenation of formed intermediate. In this reaction, the amount and size of Pt nanoparticles on catalysts are important factors. The catalyst containing 0.2 wt% Pd, with a relatively large amount of Pt atoms and a small Pt particle size (<4 nm), exhibits the highest activity and selectivity of benzimidazole synthesis.

In Chapter II, TiO₂ loaded with Pd nanoparticles (Pd/TiO₂) was used for photocatalytic reaction of aromatic cyanide with ethanol under UV irradiation (λ > 300 nm). This catalytic system successfully promoted hydrodenitrogenation of aromatic cyanides and produced toluene derivatives with high selectivity at room temperature. This reaction proceeds by photocatalytic oxidation of ethanol to produce acetaldehyde and hydrogen atom on the Pd surface (H-Pd species). The H-Pd species promotes hydrodenitrogenation of aromatic cyanides and subsequent condensation with aldehydes, leading to successful hydrodenitrogenation. The catalytic activity strongly depends on the amount of Pd loaded. The catalyst containing 2 wt% Pd, with a relatively low Schottky barrier height at the Pd/TiO₂ heterojunction and a large number of surface Pd atoms, exhibits the highest denitrogenation activity.

In Chapter III, the author studied N-alkylation of primary amines with alcohols in the presence of metal-loaded TiO₂ under photoirradiation (λ > 300 nm). The author found that TiO₂ loaded with Pd nanoparticles successfully promotes N-monoalkylation of primary amines at room temperature. This reaction proceeds via three consecutive steps involving (i) Pd-assisted photocatalytic oxidation of alcohols; (ii) catalytic condensation of the formed aldehyde and amine on the TiO₂ surface; and, (iii) catalytic hydrogenation of the formed imine on Pd nanoparticles. The catalyst with 0.3 wt% Pd, containing 2–2.5 nm Pd particles, shows the highest activity for imine hydrogenation, and smaller or larger Pd particles are inefficient.

In Chapter IV, the author found that TiO₂ loaded with bimetallic Pd-Pt alloy nanoparticles (PdPt/TiO₂) promotes highly efficient photocatalytic dehalogenation of organic halides with alcohol as a
hydrogen source. The activity is more than three times that of TiO₂ loaded with Pd particles and higher than the conventional method with molecular hydrogen. The high activity is due to the enhancement consumption of photoformed e⁻ on the Pt site by H⁺ reduction and efficient transfer of the formed hydrogen atom to the adjacent Pd site within the alloy particles.

In Chapter V, WO₃ loaded with Pt nanoparticles (Pt/WO₃) were employed for photocatalytic oxidation of cyclohexane with molecular oxygen under visible light irradiation (λ >420 nm) to produce cyclohexanol and cyclohexanone. The catalysts successfully promote partial oxidation with ca. 93% selectivity, without the formation of subsequent decomposition of these products. The ESR measurement with a spin trapping reagent and the photocatalytic reaction with a superoxide radical scavenger indicate that selective oxidation of cyclohexane on the catalysts is indeed achieved due to the decreased formation of superoxide radicals that promotes decomposition of the products.

In chapter VI, the author found that Pt nanoparticles loaded on anatase TiO₂, when used for aerobic oxidation under visible light (λ >450 nm), facilitate direct e⁻ transfer to anatase and promote the reaction highly efficiently. This occurs via the electronic excitation of Pt particles by visible light followed by the transfer of their e⁻ to anatase conduction band. The positively charged Pt particles oxidize substrates. Whereas the conduction band e⁻ are consumed by the reduction of molecular oxygen. The catalyst loaded with 2 wt% Pt, containing 3-4 nm Pt particles, creates a relatively low Schottky barrier and a relatively large number of perimeter Pt atoms and, hence, facilitates smooth Pt→anatase e⁻ transfer, resulting in very high photocatalytic activity.

The results obtained in this work are summarized in general conclusions. Suggestions for future work are described as an extension of the present work.

Reference


2004, 3, 859.


Chapter I

Synthesis of benzimidazoles on TiO\textsubscript{2} Loaded with Pt Nanoparticles

1. Introduction

Benzimidazole and its derivatives occupy pivotal positions in the synthesis of natural products and pharmaceutical materials. These compounds have been studied extensively because of their biological activities as bactericides,\textsuperscript{1} anticarcinogens,\textsuperscript{2} and peptic ulcer agents.\textsuperscript{3} There is particular interest in their activity against several viruses such as HIV,\textsuperscript{4} herpes (HSV-1),\textsuperscript{5} and influenza.\textsuperscript{6} Classical method for benzimidazole synthesis is the coupling of \(o\)-arylenediamines with carboxylic acids or their derivatives,\textsuperscript{7} which requires strong acidic conditions and high temperature (ca. \(>200^\circ\text{C}\)). The other method is the oxidation of benzimidazoline intermediates generated from the condensation of \(o\)-arylenediamines and aldehydes.\textsuperscript{8} This method produces benzimidazoles at relatively low temperature (\(~100^\circ\text{C}\)), but requires unstable aldehydes as reactants and stoichiometric or excess amounts of strong oxidants such as DDQ. Recent advances in this method allow the use of molecular oxygen as an oxidant,\textsuperscript{9} but these processes require homogeneous catalysts such as metal triflates and a free radical. Alternative methods that proceed under mild reaction conditions with stable reactants such as alcohols and carboxylic acids and easy-handling heterogeneous catalysts are therefore necessary for economically and environmentally benign benzimidazole production.

Here we present a new strategy for benzimidazole synthesis without acids and oxidants at room temperature (Scheme 1-1). This promotes efficient and selective benzimidazole production with \(o\)-arylenediamines and alcohols as reactants under photoirradiation (\(\lambda \geq 300\ \text{nm}\)). The process employs a semiconductor TiO\textsubscript{2} loaded with Pt nanoparticles (Pt/TiO\textsubscript{2}) as a heterogeneous catalyst. The catalyst promotes two different transformations in one pot by simultaneous photocatalytic and catalytic actions; one is the conversion of alcohols to aldehydes via a Pt-assisted photocatalytic oxidation on the TiO\textsubscript{2} surface,\textsuperscript{10} and the other is the catalytic dehydrogenation of benzimidazoline intermediates, generated from the condensation of \(o\)-arylenediamines and aldehydes, on the surface of Pt particles. Various catalytic systems enabling one-pot organic transformations have been proposed.\textsuperscript{11} There are, however, only two reports of one-pot system that combines photocatalysis and catalysis,\textsuperscript{12} where both systems use a set of homogeneous photocatalyst (photoredox catalyst) and catalyst for one-pot transformations.
Scheme 1-1. One-pot benzimidazole synthesis with Pt/TiO₂ catalyst under photoirradiation.

2. Experimental
2-1. Materials and procedure

All of the reagents used were supplied from Wako, Tokyo Kasei, and Sigma-Aldrich and used without further purification. Water was purified by the Milli-Q system. JRC-TIO-4 TiO₂ (equivalent to Degusa P25; particle diameter, 24 nm; BET surface area, 54 m² g⁻¹; anatase/rutile = ca. 83/17) were kindly supplied from the Catalyst Society of Japan.

The Pt/TiO₂ catalyst [x (wt%) = Pt/(Pt + TiO₂) × 100; x = 0.05, 0.1, 0.2, 0.5, 1.0] were synthesized as hollows: TiO₂ (0.1 g) and H₂PtCl₆ (0.1, 0.21, 0.42, 1.06, and 2.12 mg) were added to a water/MeOH (24/1 v/v) mixture (10 mL) within a Pyrex glass tube (20 cm³) and purged with nitrogen gas. The tube was photoirradiated with magnetic stirring by a high-pressure Hg lamp (300 W; Eikohsha Co. Ltd.; light intensity at 300-400 nm, 19.1 W m⁻²) at 303 K for 30 min. The resultant was recovered by filtration, washed thoroughly with water, and dried in vacuo at 353 K for 12 h. The Pt amount on the catalysts was determined by X-ray fluorescence spectrometer.

Photoreaction were carried out as follows; o-arylenediamine, alcohol, and catalyst were added to a Pyrex glass tube (20 cm³). The tube was purged with nitrogen gas and photoirradiated with magnetic stirring by a Xe lamp (2 kW; Ushio Inc.; light intensity, 18.2 W m⁻² at 300-400 nm) at 303 K. The reactant and product concentrations were determined by GC systems equipped with FID or TCD.

Intermediate 3 (1-(1-ethoxyethyl)-2-methyl-1H-benzimidazole) were synthesized as hollows: An EtOH solution containing 1 was photoirradiated in the presence of pure TiO₂ for 12 h at 303 K. The resulting solution was concentrated by evaporation and subjected to flash chromatography using silica gel with ethyl acetate as an eluent. The obtained solution was concentrated by evaporation and dried in vacuo, affording a yellow crystal of 3. ¹H NMR (400 MHz, CDCl₃, TMS): δ (ppm) = 7.69–7.66 (q, 1H), 7.60–7.58 (q, 1H), 7.23–7.17 (m, 2H), 5.67–5.62 (q, 1H), 3.43–3.25 (m, 2H), 2.63 (s, 3H), 1.73–1.72 (d, 3H), 1.17–1.14 (t, 3H). ¹³C NMR (400 MHz, CDCl₃, TMS): δ (ppm) = 150.38, 142.68, 133.29, 122.08, 121.85, 118.94, 111.18, 82.82, 63.82, 21.32, 14.82, 14.74. EI-MS: Calcd for C₁₂H₁₆N₂O 204.3, found m/z 204.2 (M⁺).
3. Results and discussion

3-1. Synthesis and characterization of catalysts

![TEM micrograph and size distribution of Pt particles on Pt0.2/TiO2.](image)

**Figure 1-4.** a) TEM micrograph and b) size distribution of Pt particles on Pt0.2/TiO2.

![TEM micrograph and size distribution of Pt nanoparticles on Pt0.3/TiO2 and Pt1.0/TiO2 catalysts.](image)

**Figure 1-5.** TEM micrograph and size distribution of Pt nanoparticles on a) Pt0.3/TiO2 and b) Pt1.0/TiO2 catalysts.
Figure 1-6. a) Diffuse reflectance UV-vis spectra and b) photographs for the respective catalysts.
Pt\textsubscript{x}/TiO\textsubscript{2} with different Pt amount \[ x \text{ (wt\%) } = \text{Pt/(TiO}_2 + \text{Pt}) \times 100; \ x = 0.05, 0.1, 0.2, 0.5, 1.0 \] were prepared by a conventional photodeposition method,\textsuperscript{13} where photoirradiation of an aqueous solution containing JRC-TIO-4 TiO\textsubscript{2} particles (equivalent to Degussa P25) and H\textsubscript{2}PtCl\textsubscript{6} affords gray powders of catalysts. Figure 1-4 shows the transmission electron microscopy (TEM) image of Pt\textsubscript{0.2}/TiO\textsubscript{2}. A spherical Pt particle is observed with an average diameter 2.0 nm. The Pt particle size increases with an increase in the Pt amount on TiO\textsubscript{2}, where \( x = 0.5 \) and 1.0 catalysts contain 4.0 nm and 9.3 nm particles, respectively (Figure 1-5). In addition, the catalysts with larger Pt amount show increased absorbance at \( \lambda >300 \text{ nm} \) due to light scattering by the Pt particles\textsuperscript{14} (Figure 1-6), although the band gap energies of the catalysts are similar (3.2–3.3 eV).

3-2. Photocatalytic activity of Pt/TiO\textsubscript{2} catalyst.

![Graph](image-url)

Figure 1-7. Time-dependent change in the concentrations of substrate and products during photoirradiation of 1 in EtOH with a) TiO\textsubscript{2} and b) Pt\textsubscript{0.2}/TiO\textsubscript{2} catalysts. Reaction conditions: catalyst (10 mg), 1 (20 \textmu mol), EtOH (10 mL), nitrogen (1 atm), \( \lambda >300 \text{ nm} \), 303 K, where 10 mg Pt\textsubscript{0.2}/TiO\textsubscript{2} contains 0.10 \textmu mol Pt.

The efficacy of Pt/TiO\textsubscript{2} catalyst on benzimidazole production is evident from the reaction of \textit{o}-phenylenediamine (1) with EtOH. Figure 1-7 shows the time-dependent change in the concentrations of 1 and the product, 2-methylbenzimidazole (2), during photoirradiation (\( \lambda >300 \text{ nm} \)) of an EtOH solution containing 1 under nitrogen atmosphere. With pure TiO\textsubscript{2} (Figure 1-7a), 24 h photoirradiation is required to achieve >90% conversion of 1, where the 2 yield is only ca. 60%. The major byproduct is
determined by $^1$H, $^{13}$C NMR and EI-MS analysis to be 1-(1-ethoxyethyl)-2-methyl-1H-benzimidazole (3) (Figures 1-1-3), where the 3 yield after 36 h irradiation is 5.2%. In contrast, as shown in Figure 1-7b, Pt$_{0.2}$/TiO$_2$ promotes rapid and selective production of 2; only 2 h irradiation achieves >99% 1 conversion and produces 2 with >93% yield. This indicates that the present process with Pt/TiO$_2$ indeed promotes rapid and selective benzimidazole production.

3-3. Reaction mechanism

\[
\text{TiO}_2 \xrightarrow{h\nu} \text{TiO}_2 (e^-, h^+) \\
\xrightarrow{2h^+} 2e^- \\
\xrightarrow{2e^-} \text{H}_2 \\
\xrightarrow{2H^+} \text{H}_2 \text{O} \\
\text{NH}_2 \text{NH}_2 \xrightarrow{\text{H}_2\text{O}} \text{H}_2 \text{N}-\text{N}=\text{H}
\]

Scheme 1-2. Proposed mechanism for one-pot benzimidazole production promoted by Pt/TiO$_2$ catalyst under photoirradiation.

The rapid and selective 2 formation is achieved by simultaneous photocatalytic and catalytic reactions on Pt/TiO$_2$, as depicted in Scheme 1-2. The reaction is initiated by photoexcitation of TiO$_2$ particles. The excited TiO$_2$ produces electron (e$^-$) and positive hole (h$^+$) pairs. The h$^+$ oxidizes EtOH to acetaldehyde on the TiO$_2$ surface.$^{15}$ Spontaneous condensation of the formed aldehyde and 1 produces a monoimine intermediate (4).$^{16}$ The rapid consumption of 1 during the reaction with Pt/TiO$_2$ (Figure 1-7b) is because the Pt particles efficiently trap e$^-$ on the excited TiO$_2$ and enhance the charge separation between e$^-$ and h$^+$.$^{17}$ This accelerates the alcohol oxidation (production of large amount of aldehyde) and thus allows rapid condensation of 1 and the aldehyde. As shown in Figure 1-7, the amount of H$_2$ produced during 12 h irradiation with Pt/TiO$_2$ is 486 $\mu$mol, whereas pure TiO$_2$ produces only 3 $\mu$mol H$_2$. 

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This indicates that the e\textsuperscript{-} formed on TiO\textsubscript{2} is indeed trapped by the Pt particles and consumed efficiently by the reduction of H\textsuperscript{+} formed during alcohol oxidation\textsuperscript{15}. These suggest that the enhanced photocatalytic transformation of alcohol to aldehyde on Pt/TiO\textsubscript{2} allows efficient production of the intermediate 4.

![Figure 1-8. Time-dependent change in the amount of 1, 2, and H\textsubscript{2} during the reaction of 1 with 1 equiv of acetaldehyde in the dark condition, a) without catalyst, b) with TiO\textsubscript{2}, and c) with Pt\textsubscript{0.2}/TiO\textsubscript{2}. Reaction conditions: catalyst (10 mg), 1 (20 \textmu mol), acetaldehyde (20 \textmu mol), EtOH (10 mL), nitrogen (1 atm), 303 K, where 10 mg Pt\textsubscript{0.2}/TiO\textsubscript{2} contains 0.10 \textmu mol Pt.](image)

The product 2 is formed by cyclization of 4 followed by autooxidation of a benzimidazoline intermediate (5) with a release of H\textsuperscript{+}\textsuperscript{18}, where 4 and 5 are in equilibrium\textsuperscript{19}. The 4 reacts easily with the other aldehyde and produces a diimine intermediate (6), leading to a byproduct (3) formation\textsuperscript{20}. Therefore, in the classical method with o-arylenediamines and aldehydes\textsuperscript{8,9} oxidants that promote rapid transformation of 5 to 2 are necessary for selective formation of 2 while suppressing byproduct formation. In the present process with Pt/TiO\textsubscript{2}, Pt particles promote rapid and selective transformation of 5 to 2 via a catalytic dehydrogenation (Scheme 1-2). This is confirmed by the reaction of 1 with equimolar acetaldehyde in the dark condition. Figure 1-8 shows the time-dependent change in the amounts of 1 and the products at 303 K. The rate of decrease of 1 with Pt/TiO\textsubscript{2} (Figure 1-8c) is similar to that obtained without catalyst and with pure TiO\textsubscript{2} (Figure 1-8a and b), indicating that the rate of condensation of 1 and aldehyde is similar. The 2 yields obtained without catalyst and with TiO\textsubscript{2} are low (<40\%), but Pt/TiO\textsubscript{2} produces 2 quantitatively, indicating that Pt particles successfully promote transformation of 5 to 2. In this case, H\textsubscript{2} gas with an equivalent quantity of 2 was produced, whereas
other systems do not produce H2. This suggests that the Pt particles indeed catalyze dehydrogenation of 5. The rapid transformation of 5 to 2 in the Pt/TiO2 system, therefore, leads to a shift of the equilibrium between 4 and 5 to the 5 formation (Scheme 1-2). This thus allows selective 2 formation while suppressing byproduct formation. The high dehydrogenation activity of Pt particles at room temperature is probably due to the strong affinity of the amine nitrogens of 5 to the Pt surface, as observed for ethylenediamine dehydrogenation on the Pt surface.21

3-4. Effect of Pt amount and size on the catalytic activity

The amount and size of Pt particles are important factors for rapid and selective benzimidazole production. Figure 1-9 shows the conversion of 1 and the selectivity of 2 during 4 h photoirradiation of an EtOH solution containing 1 with respective catalysts. Conversion of 1 increases with an increase in the Pt amount on TiO2 because larger amount of Pt allows efficient charge separation on the photoexcited TiO2. The highest conversion is obtained with Pt0.2/TiO2, and the catalysts with larger Pt amount show lower conversion. This is because excess amount of Pt suppresses the incident light absorption by TiO2.22

![Figure 1-9](image)

**Figure 1-9.** Conversion of 1 and selectivity of 2 obtained by photoirradiation of an EtOH solution containing 1 with TiO2 and Pt_{x}/TiO2 catalysts for 4 h. Reaction conditions: EtOH (10 mL), 1 (0.1 mmol), catalyst (10 mg), nitrogen (1 atm), \(\lambda >300\) nm, 303 K.

The 2 selectivity is also affected by the Pt amount. As shown in Figure 1-9, the selectivity increases with an increase in the Pt amount, but the catalysts with >0.2 wt% Pt show lower selectivity. This is because larger size Pt particles have lower dehydrogenation activity. As reported,23 dehydrogenation
activity of Pt particles increases with a decrease in their size; in particular, <4 nm particles show very high activity. The size of Pt particles on Pt\textsubscript{0.2}/TiO\textsubscript{2} is 2.0 nm, whereas that on x = 0.5 and 1.0 catalysts are 4.0 and 9.3 nm, respectively. As shown in Table 1-1, the reaction of 1 and equimolar acetaldehyde in the dark with Pt\textsubscript{0.2}/TiO\textsubscript{2} (4 h, 303 K) produces 2 with 91% yield, along with 82% H\textsubscript{2} formation. In contrast, x = 0.5 and 1.0 catalysts show lower yields of 2 (<80%) and H\textsubscript{2} (<48%). This indicates that smaller Pt particles with a <4 nm diameter indeed have higher dehydrogenation activity and are responsible for efficient benzimidazole formation. TEM analysis of Pt\textsubscript{0.2}/TiO\textsubscript{2} recovered after 12 h photoreaction for 2 synthesis (Figure 1-7b) reveals that the Pt particle size scarcely changes during the reaction (Figure 1-10). In addition, the catalyst is reusable at least three times without loss of activity (Table 1-2).

**Table 1-1.** Conversion and product yields obtained by the reaction of 1 with acetaldehyde in the presence of various catalysts in the dark condition.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Pt particle size / nm</th>
<th>Conversion / %</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO\textsubscript{2}</td>
<td></td>
<td>96</td>
<td>69</td>
</tr>
<tr>
<td>2</td>
<td>Pt\textsubscript{0.05}/TiO\textsubscript{2}</td>
<td>&gt;99</td>
<td>86</td>
<td>59</td>
</tr>
<tr>
<td>3(^c)</td>
<td>Pt\textsubscript{0.05}/TiO\textsubscript{2}</td>
<td>&gt;99</td>
<td>89</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>Pt\textsubscript{0.1}/TiO\textsubscript{2}</td>
<td>98</td>
<td>91</td>
<td>65</td>
</tr>
<tr>
<td>5(^d)</td>
<td>Pt\textsubscript{0.1}/TiO\textsubscript{2}</td>
<td>&gt;99</td>
<td>92</td>
<td>84</td>
</tr>
<tr>
<td>6</td>
<td>Pt\textsubscript{0.2}/TiO\textsubscript{2}</td>
<td>2.0(^e)</td>
<td>&gt;99</td>
<td>91</td>
</tr>
<tr>
<td>7</td>
<td>Pt\textsubscript{0.3}/TiO\textsubscript{2}</td>
<td>4.0(^e)</td>
<td>&gt;99</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>Pt\textsubscript{1.5}/TiO\textsubscript{2}</td>
<td>9.3(^e)</td>
<td>97</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>TiO\textsubscript{2} + Pt black</td>
<td>3400(^f)</td>
<td>93</td>
<td>77</td>
</tr>
</tbody>
</table>

\(^a\) Reaction condition: Catalyst (10 mg), 1 (0.1 mmol), acetaldehyde (0.1 mmol), EtOH (10 mL), nitrogen (1 atm), reaction time (4 h), 303 K. \(^b\) The amount of H\textsubscript{2} formed is less than detection limit (<0.12 \textmu mol). \(^c\) catalyst (40 mg). \(^d\) catalyst (20 mg). \(^e\) determined by TEM analysis. \(^f\) determined by dynamic light scattering measurement.
**Figure 1-10.** Size distribution of Pt nanoparticles on (black bar) fresh Pt$_{0.2}$/TiO$_2$ and (white bar) Pt$_{0.2}$/TiO$_2$ recovered after 12 h photoreaction with 1 (Figure 2b).

### Table 1-2. Reuse of Pt$_{0.2}$/TiO$_2$ catalyst for 2 synthesis.\(^{a}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion / %</th>
<th>Yield / %</th>
</tr>
</thead>
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<td>1</td>
<td>Fresh</td>
<td>&gt;99</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>1st reuse</td>
<td>&gt;99</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>2nd reuse</td>
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<td>95</td>
</tr>
<tr>
<td>4</td>
<td>3rd reuse</td>
<td>&gt;99</td>
<td>94</td>
</tr>
</tbody>
</table>

\(^{a}\) Reaction conditions: catalyst (10 mg), 1 (20 µmol), EtOH (10 mL), nitrogen (1 atm), \(\lambda >300\) nm, 303 K, photoirradiation time (12 h).

### 3.5. Synthesis of various benzimidazole

The present process is tolerant for synthesis of various kinds of benzimidazoles. As shown in Table 1-3, photoirradiation of alcohol solutions containing various \(o\)-arylenediamines with Pt$_{0.2}$/TiO$_2$ successfully produces the corresponding benzimidazoles. In that, 2-alkyl- and 2-aryl-substituted benzimidazoles are produced with very high yields. In addition, 5- and/or 6-substituted derivatives are also produced successfully.
Table 1-3. Synthesis of benzimidazoles from o-arylenediamines and alcohols.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Diamines</th>
<th>Amount / (\mu)mol</th>
<th>Alcohol</th>
<th>(t) / h</th>
<th>Catalyst</th>
<th>Diamine conv. / %</th>
<th>Product</th>
<th>GC yield / %</th>
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<td>1</td>
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<td>20</td>
<td></td>
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<td>(\text{TiO}_2)</td>
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<td>(\text{H}N\text{N})</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>20</td>
<td>-OH</td>
<td>4</td>
<td>(\text{PtO}_2/\text{TiO}_2)</td>
<td>&gt;99</td>
<td>(\text{H}N\text{N})</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>20</td>
<td>-OH</td>
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<td>(\text{TiO}_2)</td>
<td>56</td>
<td>(\text{H}N\text{N})</td>
<td>34</td>
</tr>
<tr>
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<td></td>
<td>20</td>
<td>-OH</td>
<td>4</td>
<td>(\text{PtO}_2/\text{TiO}_2)</td>
<td>&gt;99</td>
<td>(\text{H}N\text{N})</td>
<td>&gt;99</td>
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<tr>
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<td>20</td>
<td>-OH</td>
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<td>(\text{TiO}_2)</td>
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<td>(\text{H}N\text{N})</td>
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<td>(\text{H}N\text{N})</td>
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<td>(\text{H}N\text{N})</td>
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<tr>
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<td>Ph.OH</td>
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<td>(\text{PtO}_2/\text{TiO}_2)</td>
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<td>(\text{H}N\text{N})</td>
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<td>(\text{H}N\text{N})</td>
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<td>20</td>
<td></td>
<td>4</td>
<td>(\text{PtO}_2/\text{TiO}_2)</td>
<td>&gt;99</td>
<td>(\text{H}N\text{N})</td>
<td>83</td>
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</tbody>
</table>

\(^a\) Reaction conditions: catalyst (10 mg), alcohol (10 mL), nitrogen (1 atm), \(\lambda > 300\) nm. \(^b\) catalyst (80 mg), alcohol (5 mL). \(^c\) catalyst (5 mg), alcohol (750 \(\mu\)mol), MeCN (5 mL).

4. Conclusion

In conclusion, we found that the Pt/TiO\(_2\) system enables efficient benzimidazole production under photoirradiation. This is promoted by one-pot multiple catalytic transformations on Pt/TiO\(_2\), which involve Pt-assisted photocatalytic oxidation on TiO\(_2\) and catalytic dehydrogenation on the surface of Pt particles. The process has significant advantages as compared to the other methods:\(^{24}\) (i) cheap and stable reactant (alcohol); (ii) no requirement of acids and oxidants; (iii) no harmful byproduct formation (only water and H\(_2\) form during reaction); (iv) mild reaction condition (room temperature). The process therefore has a potential to enable green benzimidazole synthesis. Recently, organic transformation with semiconductor photocatalysts has attracted much attention,\(^{25}\) but successful examples are still scarce. The basic idea presented here based on the combination of photocatalytic and catalytic reactions may help open a new strategy towards the development of photocatalysis-based organic synthesis.
Figure 1-11. Time-dependent change in the concentrations of o-dinitrobenzene and the product 2 during photoirradiation of an EtOH solution containing o-dinitrobenzene. Reaction conditions: Degussa P25 TiO₂ (10 mg), o-dinitrobenzene (20 µmol), EtOH (10 mL), nitrogen (1 atm), λ >300 nm (Xe lamp; 2 kW; Ushio Inc.; light intensity, 18.2 W m⁻² at 300–400 nm), 303 K.

5. References
[9] (a) Chen, Y.-X.; Qian, L.-F.; Zhang, W.; Han, B. Angew. Chem. Int. Ed. 2008, 47, 9330. (b) Trivedi,
[24] There is one report of photocatalytic benzimidazole production process, consisting of photoirradiation of an alcohol solution containing o-dinitrobenzenes with pure Degussa P25 TiO2: Wang, H.; Partch, R. E.; Li, Y. J. Org. Chem. 1997, 62, 5222. However, the benzimidazole selectivity is only ca. 25% (Figure 1-11).
Chapter II

Hydrodenitrogenation of Aromatic Cyanides on TiO$_2$ Loaded with Pd Nanoparticles

1. Introduction

Aromatic cyanides are one of the most important chemicals used as solvents, extractants, and intermediates for the synthesis of pharmaceuticals, plastics, rubbers, herbicides, and pesticides. These compounds are therefore often contained in industrial effluents. Since they are highly toxic to living organisms, their decomposition and detoxification are very important tasks. Bioremediation processes have been studied for the treatment of aromatic cyanides. These processes decompose the compounds into harmless ones such as CO$_2$ and H$_2$O; however, they require restricted operation conditions in pH and temperature. Photocatalytic decomposition of aromatic cyanides has also been studied with titanium dioxide (TiO$_2$). Photoirradiation of TiO$_2$ in water under O$_2$ produces active oxygen species such as hydroxyl radical (OH$^+$) or superoxide anion (O$_2$•$^-$), and decomposes aromatic cyanides into CO$_2$, NO$_3^-$, and H$_2$O. These oxidative processes, however, completely decompose the aromatic nuclei of the compounds. Selective decomposition of the –CN moiety and the reuse of resulting aromatic nuclei for upstream processes are desirable for development of green and sustainable processes.

Supported Pd nanoparticles are often employed for catalytic hydrogenation of various compounds such as olefins and nitro compounds, with molecular hydrogen (H$_2$) as a hydrogen source. Hydrogenation of aromatic cyanides on Pd catalysts has also been studied at elevated temperatures. These compounds are successfully converted to toluene derivatives and NH$_3$ via hydrogenation and subsequent cleavage of C–N moiety. This hydrodenitrogenation is promoted by the reaction of aromatic cyanides with activated hydrogen species (H–Pd), formed via a dissociative adsorption of H$_2$ on the surface of Pd particles. The reaction proceeds selectively without decomposition of aromatic nuclei and enables the reuse of products for upstream processes.

Photoexcitation of semiconductor materials loaded with noble metal particles creates a positive hole (h$^+$) and conduction band electrons (e$^-$), and allows subsequent e$^-$ transfer to the metal particles. Photoexcitation of semiconductor loaded with Pd particles, when performed in protic solvents such as alcohols, produces aldehyde via oxidation of alcohol by h$^+$ and H–Pd species via reduction of protons (H$^+$) by e$^-$ on the Pd particles. This photocatalytic reaction, if performed out with aromatic cyanides, may successfully promote hydrodenitrogenation by the photoformed H–Pd species at room temperature.

In the present work, TiO$_2$ loaded with Pd particles (Pd/TiO$_2$) was used for photocatalytic reaction of...
aromatic cyanide with ethanol under UV irradiation ($\lambda > 300$ nm). This catalytic system successfully promotes hydrodenitrogenation of aromatic cyanides and produces toluene derivatives with high selectivity at room temperature. The denitrogenation mechanism was clarified, and the effect of Pd amount on the catalytic activity was studied.

2. Experimental

2-1. Materials

All of the reagents used were purchased from Wako, Tokyo Kasei, and Sigma-Aldrich, and used without further purification. Water was purified by the Milli Q system. JRC-TIO-4 TiO$_2$ (equivalent to Degussa P25; particle diameter, 24 nm; BET surface area, 54 m$^2$ g$^{-1}$; anatase/rutile = ca. 83/17) were kindly supplied from the Catalyst Society of Japan.

The Pd/TiO$_2$ catalysts [$x$ (wt%) = Pd/(Pd + TiO$_2$) × 100; $x = 0.5, 1, 2, 4$] were prepared according to literature procedure,$^{16}$ as follows: TiO$_2$ (1.0 g) and Pd(NO$_3$)$_2$ (10.9, 21.9, 44.2, or 90.2 mg) were added to water (40 mL) and solvent were evaporated with vigorous stirring at 353 K for 12 h. The obtained powders were calcined at 673 K under air flow (0.5 L min$^{-1}$) and then reduced at 673 K under H$_2$ flow (0.2 L min$^{-1}$). The heating rate and holding time at 673 K for these treatments were 2 K min$^{-1}$ and 2 h, respectively. Ag$_2$/TiO$_2$ and Pt$_2$/TiO$_2$ were prepared in a similar manner to those for Pd$_x$/TiO$_2$, using AgNO$_3$ (16 mg) or H$_2$PtCl$_6$•6H$_2$O (54 mg) as precursors.

Au$_2$/TiO$_2$ was prepared by a deposition-precipitation method, as follows:$^{17}$ HAuCl$_4$•4H$_2$O (45.8 mg) was added to water (50 mL). The pH of the solution was adjusted to 7 by an addition of 1 M NaOH. TiO$_2$ (1.0 g) was added to the solution and stirred vigorously at 353 K for 3 h. The particles were recovered by centrifugation and washed with water. They were calcined at 673 K under air flow (0.5 L min$^{-1}$).

2-2. Photoreaction procedure

Each of the respective catalysts (10 mg) was added to ethanol (5 mL) containing aromatic cyanides within a Pyrex glass tube (20 cm$^3$; $\phi$16.5 mm). The tube was sealed using a rubber septum cap and purged with argon gas. Each tube was photoirradiated with magnetic stirring by a Xe lamp (2 kW; Ushio Inc.). The temperature of solution during photoirradiation was 298 K, and the light intensity was 18.2 W m$^{-2}$ (at 300–400 nm; through a water filter). After photoirradiation, the gas phase product was analyzed by GC-TCD (Shimadzu; GC-8A). The resulting solution was recovered by centrifugation and analyzed by GC-FID (Shimadzu; GC-2010), where the products were identified by GC-MS (EI) (Shimadzu; 40
2.3. Analysis

Total amounts of metals on the catalysts were determined by an inductively-coupled argon plasma atomic emission spectrometer (ICAP-AES; SII Nanotechnology, SPS 7800), after dissolution of catalysts in an aqua regia. Diffuse reflectance UV-vis spectra were measured on a UV-vis spectrophotometer (Jasco Corp.; V-550 with Integrated Sphere Apparatus ISV-469) using BaSO₄ as a reference. Transmission electron microscopy (TEM) observations were carried out using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV.

3. Results and discussion

3.1. Synthesis and characterization of catalysts

The Pdₓ/TiO₂ catalysts with different Pd loadings \[ x \text{ (wt\%)} = \frac{\text{Pd}}{\text{Pd} + \text{TiO}_2} \times 100; x = 0.5, 1, 2, 4 \] were prepared by impregnation of Pd(NO₃)₂ onto TiO₂ followed by reduction with H₂. Figure 2-1 shows the typical TEM images of respective Pdₓ/TiO₂ catalysts. All catalysts contain spherical Pd particles. The size of Pd particles increases with the Pd loadings: the average diameters for \( x = 0.5, 1, 2, \) and 4 catalysts were 2.6, 4.1, 5.0, and 6.5 nm, respectively. As shown in Figure 2-2, the high-resolution TEM images of catalysts revealed that Pd particles can be indexed as fcc structures, as same as bulk metallic Pd (JCPDS 46-1043). Figure 2-3 shows the diffuse reflectance UV-vis spectra of catalysts. The higher Pd loading catalysts exhibit increased absorbance at \( \lambda > 300 \text{ nm} \), due to the light scattering by the Pd particles. As shown in inset, TiO₂ loaded with 2 wt% Pt (Pt₂/TiO₂) exhibits spectra similar to that of Pdₓ/TiO₂, and TiO₂ loaded with 2 wt% Au (Au₂/TiO₂) and Ag (Ag₂/TiO₂) exhibit distinctive absorption bands at 400-500 nm assigned to localized surface plasmon resonance.
Figure 2-1. TEM images and size distribution of Pd particles for (a) Pd$_{0.5}$/TiO$_2$, (b) Pd$_1$/TiO$_2$, (c) Pd$_5$/TiO$_2$, and (d) Pd$_4$/TiO$_2$ catalysts. The black bars show the data for fresh catalysts, and the white bars show the data for catalysts recovered after the 3rd reuse for reactions (Table 2, run 4).
Figure 2-2. High-resolution TEM images of Pd$_4$/TiO$_2$ catalyst. (a) The incident beam direction is [0, −1, 1]. (b) This particle is twinned particle. The incident beam directions are [0, −1, 1] and [0, 1, −1].

Figure 2-3. Diffuse-reflectance UV-vis spectra of Pd$_4$/TiO$_2$, Pd$_2$/TiO$_2$, Pd$_1$/TiO$_2$, and Ag$_2$/TiO$_2$ catalysts.

Catalytic activity of Pd/TiO$_2$ for hydrodenitrogenation was studied with benzonitrile (1) as a model compound. Table 2-1 (runs 1–3) summarizes the results for hydrodenitrogenation of benzonitrile with H$_2$ (1 atm) as a hydrogen source in the dark. Benzonitrile (2 mM) and Pd$_4$/TiO$_2$ (10 mg) were added to an n-hexane solution (5 mL) containing 5% ethanol, and the solution was stirred under H$_2$ (1 atm) for 6 h at different temperature. As shown in run 1, the benzonitrile conversion at 298 K is 84% but the yield of toluene (2) is only 15%, where large amounts of benzylamine (3, 30%) and N-ethylbenzylamine (4, 38%) remain. This suggests that the C–N cleavage is difficult to achieve at this temperature. As shown in runs 2 and 3, the rise in temperature increases the toluene yields, and the reaction at 333 K facilitates almost quantitative conversion to toluene (run 3). Photocatalytic reaction of benzonitrile with alcohol as a hydrogen donor was carried out. The reaction was performed by photoirradiation (λ >300 nm) of the
solution under argon (1 atm) for 6 h. As shown in run 4, the reaction facilitates complete conversion of benzonitrile to toluene at 298 K. This suggests that photocatalytic reaction with alcohol as a hydrogen source successfully promotes hydrodenitrogenation even at room temperature.

### Table 2-1. Hydrodenitrogenation of benzonitrile with Pd₂/TiO₂ catalyst.

<table>
<thead>
<tr>
<th>Run</th>
<th>System</th>
<th>Temperature / K</th>
<th>Conversion of 1 / %</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1⁵</td>
<td>H₂</td>
<td>298</td>
<td>84</td>
<td>15 30 38</td>
</tr>
<tr>
<td>2</td>
<td>H₂</td>
<td>313</td>
<td>98</td>
<td>61 14 23</td>
</tr>
<tr>
<td>3</td>
<td>H₂</td>
<td>333</td>
<td>&gt;99</td>
<td>99 0 0</td>
</tr>
<tr>
<td>4⁶</td>
<td>Photo</td>
<td>298</td>
<td>99</td>
<td>99 0 0</td>
</tr>
</tbody>
</table>

* Dibenzylamine (1%) was also detected as a product. This is produced by nucleophilic attack of a lone pair of nitrogen atom of benzylamine to an electrophilic carbon of semi-hydrogenated intermediate (ref 13). After photoreaction, acetaldehyde (197 μmol) and trace amount of N,N-diethylbenzylamine (5) were formed.

### 3-2. Photocatalytic activity of Pd/TiO₂ catalysts

Photocatalytic activity of Pd₂/TiO₂ with different Pd loadings (x) was studied in ethanol. Table 2-2 summarizes the results for photocatalytic reaction of benzonitrile by 6 h reaction. As shown in run 1, pure TiO₂ promotes almost no reaction of benzonitrile. In contrast, increased Pd loadings (runs 2–5) enhances reaction and produces toluene with high selectivity (>95%). Among the catalysts, Pd₂/TiO₂ exhibits the highest denitrogenation activity, and further Pd loading (Pd₄/TiO₂) decreases the activity. Loading of other metal particles is inefficient for denitrogenation. As shown in runs 6 and 7, Au₂/TiO₂ or Ag₂/TiO₂ promotes almost no reaction of benzonitrile. Pt₂/TiO₂ (run 8) shows relatively high conversion of benzonitrile (45%); however, the toluene yield is only 8%, where N,N-diethylbenzylamine (5) is produced mainly (36%). These data indicate that Pd/TiO₂ catalyst, especially loaded with 2 wt% Pd, promotes efficient denitrogenation. It must be noted that the catalyst is reusable for further reaction. As shown in run 4, the Pd₂/TiO₂ catalyst, when reused for further reaction, shows activity and selectivity.
similar to those of virgin catalyst. In addition, as shown in Figure 2-1c (white bars), TEM analysis of the catalyst recovered after the reaction revealed that the size of Pd particles scarcely changes during the reactions. This indicates that the catalyst is reusable without loss of activity and selectivity.

As shown in runs 2–5 (Table 2-2), photoreactions with Pd/TiO₂ catalysts produced triethylamine (6) with the amount similar to that of toluene formed. Figure 2-4 shows the time-dependent change in the amounts of benzonitrile and products during photoreaction with Pd₂/TiO₂ catalyst. Photoirradiation leads to a decrease in the amount of benzonitrile, along with a formation of toluene and triethylamine. The profile for the toluene formation is very similar to that for the triethylamine formation. These data clearly suggest that the nitrogen atom of benzonitrile is removed as triethylamine.

<p>| Table 2-2. Photocatalytic hydrodenitrogenation of benzonitrile (1) in ethanol with various catalysts.⁹ |
|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>d / nm&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Conversion of 1 / %</th>
<th>Yield / %</th>
<th>Acetaldehyde formed / µmol</th>
<th>H₂ formed / µmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Pd₅/TiO₂</td>
<td>2.6</td>
<td>42</td>
<td>40</td>
<td>trace</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>Pd₁/TiO₂</td>
<td>4.1</td>
<td>58</td>
<td>57</td>
<td>trace</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>Pd₂/TiO₂</td>
<td>5.0</td>
<td>&gt;99</td>
<td>98</td>
<td>trace</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1st reuse&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td>&gt;99</td>
<td>99</td>
<td>trace</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>2nd reuse&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td>&gt;99</td>
<td>97</td>
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<td>5.1</td>
<td>&gt;99</td>
<td>98</td>
<td>trace</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>Pd₄/TiO₂</td>
<td>6.5</td>
<td>86</td>
<td>85</td>
<td>trace</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>Au₂/TiO₂</td>
<td>3.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Ag₂/TiO₂</td>
<td>4.6</td>
<td>0</td>
<td>0</td>
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<td>8</td>
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<td>3.1</td>
<td>45</td>
<td>8</td>
<td>36</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>Pd₃/TiO₂&lt;sup&gt;d&lt;/sup&gt;</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: catalyst (10 mg), benzonitrile (10 µmol), ethanol (5 mL), Xe lamp (λ >300 nm), Ar (1 atm), temperature (298 K), photoirradiation time (6 h).<sup>b</sup> Average diameter for metal nanoparticles determined by TEM observations. <sup>c</sup> Catalysts were reused after simple washing with ethanol.<sup>d</sup> Photoreaction was performed without benzonitrile.
Figure 2-4. Time-dependent change in the amounts of benzonitrile (1) and the products obtained during photoreaction of benzonitrile with Pd\textsubscript{2}/TiO\textsubscript{2} catalyst. Reaction conditions are identical to those in Table 2-2.

3-3. Mechanism for photocatalytic hydrodenitrogenation

Photocatalytic hydrodenitrogenation of benzonitrile is initiated by photoexcitation of TiO\textsubscript{2}. This produces the positive hole (h\textsuperscript{+}) and electron (e\textsuperscript{-}) pairs, as follows.

\[ \text{TiO}_2 + h\nu \rightarrow h^+ + e^- \]  \hspace{1cm} (1)

The h\textsuperscript{+} oxidizes ethanol and produces acetaldehyde and protons (H\textsuperscript{+}) on the TiO\textsubscript{2} surface\textsuperscript{18,20}.

\[ \text{CH}_3\text{CH}_2\text{OH} + 2h^+ \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ \]  \hspace{1cm} (2)

The photoformed conduction band e\textsuperscript{-} is transferred to the Pd particles. This reduces H\textsuperscript{+} and produces a hydrogen atom on the particles (H–Pd species).

\[ \text{H}^+ + e^- + \text{Pd} \rightarrow \text{H–Pd} \]  \hspace{1cm} (3)

The parts of the hydrogen atoms on the Pd particles are removed by the coalescence as a H\textsubscript{2} gas.

\[ \text{H–Pd} + \text{H–Pd} \rightarrow \text{H}_2\uparrow + 2\text{Pd} \]  \hspace{1cm} (4)

The stoichiometrical conversion of benzonitrile to toluene and triethylamine (Figure 2-4) indicates that three aldehyde molecules formed by photocatalytic oxidation of ethanol (eq. 2) are involved in the hydrodenitrogenation of one benzonitrile molecule. The reaction mechanism can therefore be summarized in Scheme 2-1, which involves twelve H–Pd species. The substrate benzonitrile (1) undergoes hydrogenation by the H–Pd species and produces benzylamine (3) intermediately. This is transformed to an imine intermediate (7) by condensation with acetaldehyde, and then converted to
N-ethylbenzylamine (4) via hydrogenation by H–Pd species. Condensation of 4 with acetaldehyde and subsequent hydrogenation by H–Pd species afford N,N-diethylbenzylamine (5). Hydrogenolysis of 5 by the H-Pd species produces toluene (2) and diethylamine (8). Condensation of 8 with acetaldehyde and subsequent hydrogenation produces triethylamine (6). During the photoreaction (Figure 2-4), trace amounts of 4 and 5 (<0.1 μmol) were detected by GC analysis. In addition, as summarized in Table 2-3, photocatalytic reactions of compounds 3, 4, or 5 as the starting materials with Pd/TiO2 catalyst also produces toluene and triethylamine with almost quantitative yields. These findings clearly support the proposed denitrogenation mechanism involving the condensation with aldehyde and the hydrogenation by the H–Pd species (Scheme 2-1). As shown in Figure 2-4, the mass balance of benzonitrile (1) and toluene (2) is almost 100% during the reaction. This suggests that the hydrogenation of 1 to 3 is the rate-determining step for this reaction sequence. Table 2-2 (run 9) shows the result of photocatalytic reaction performed in the absence of benzonitrile. The photoreaction produces 248 μmol H₂, which is larger than that obtained with benzonitrile (176 μmol, run 4). This indicates that hydrodenitrogenation and H₂ evolution (eq. 4) take place competitively.

Scheme 2-1. Proposed mechanism for photocatalytic hydrodenitrogenation of benzonitrile with Pd/TiO2 catalyst in the presence of acetaldehyde.

| Table 2-3. Results of photocatalytic reaction of various substrates with Pd/TiO2 catalyst.|
|---|---|---|---|
| Substrate | Conversion / % | Yield / % |
| | | Toluene (2) | Triethylamine (6) |
| 3 | >99 | 99 | 97 |
| 4 | >99 | 99 | 98 |
| 5 | >99 | >99 | 97 |

* Reaction conditions: Pd/TiO2 (10 mg), substrate (10 μmol), ethanol (5 mL), Xe lamp (λ >300 nm), Ar (1 atm), temperature (298 K), photoirradiation time (6 h).
3-4. Hydrodenitrogenation of substituted benzonitrile

The Pd/TiO₂ catalyst was employed for hydrodenitrogenation of aromatic cyanides with several substituents. The results are summarized in Table 2-4. As shown in run 2, terephthalonitrile is successfully transformed to p-xylene with 98% yield via the hydrodenitrogenation of two −CN groups. Reaction of 1-naphthonitrile (run 3) produces 1-methylnaphthalene with 93% yield. Reactions of benzonitrile with methyl, methoxy, or hydroxyl substituents (runs 4–6) produce the corresponding toluene derivatives while maintaining these substituents. In contrast, halogen or carbonyl substituent also undergoes reaction. As shown in run 7, the reaction of p-chlorobenzonitrile produces toluene because the halogen groups are removed via the reaction with H–Pd species.¹⁵ In addition, carbonyl substituent is converted to the hydroxyl group (run 8) due to the reduction by the H–Pd species. These results suggest that the Pd/TiO₂ catalyst promotes hydrodenitrogenation of −CN group even in the presence of substituents, although some substituents are also transformed during the reaction.

Table 2-4. Results of photocatalytic hydrodenitrogenation of various aromatic cyanides with Pd₂/TiO₂ catalyst.⁴

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Time / h</th>
<th>Substrate conversion / %</th>
<th>Product</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Structure" /></td>
<td>12</td>
<td>&gt;99</td>
<td><img src="image2" alt="Structure" /></td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Structure" /></td>
<td>48</td>
<td>&gt;99</td>
<td><img src="image4" alt="Structure" /></td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="Structure" /></td>
<td>24</td>
<td>&gt;99</td>
<td><img src="image6" alt="Structure" /></td>
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<td>12</td>
<td>&gt;99</td>
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<td>12</td>
<td>&gt;99</td>
<td><img src="image10" alt="Structure" /></td>
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<td>48</td>
<td>&gt;99</td>
<td><img src="image12" alt="Structure" /></td>
<td>99</td>
</tr>
<tr>
<td>7</td>
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<td>&gt;99</td>
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<td><img src="image15" alt="Structure" /></td>
<td>12</td>
<td>&gt;99</td>
<td><img src="image16" alt="Structure" /></td>
<td>99</td>
</tr>
</tbody>
</table>

¹ Reaction conditions: Pd₂/TiO₂ (10 mg), substrate (10 μmol), ethanol (5 mL), Xe lamp (λ >300 nm), Ar (1 atm), temperature (298 K).
The Hammett plot analysis was carried out to clarify the effect of substituents on the reaction kinetics. Photocatalytic reactions of the above p-substituted benzonitriles were carried out with Pd_2/TiO_2 for 1 h, and the first-order rate constants for the decrease in substrate concentration, k (mM h^{-1}), were determined. Figure 2-5 shows the relationship between logk and the substituent constant, σ. A linear correlation is observed, and the slope of the plot (ρ) is determined to be +0.795. The positive ρ value indicates that stabilization of negative charge in the transition state efficiently promotes the reaction; in other words, the reaction proceeds via a nucleophilic attack by a nucleophile. As proposed in Scheme 2-1, the reaction of benzonitrile (1) would occur via the hydrogenation of –CN group (formation of benzylamine 3), via the nucleophilic attack by the H–Pd species. The Hammett plot results clearly support this mechanism.

![Figure 2-5](image)

**Figure 2-5.** Hammett plot for the photocatalytic reaction of p-substituted benzonitriles with Pd_2/TiO_2. The k denotes the first-order rate constant for the decrease in substrate concentration (mM h^{-1}) determined by 1 h photoreaction. The reaction conditions are identical to those in Table 2-4.

### 3-5. Effect of Pd amount on the catalytic activity

As shown in Table 2-2, the denitrogenation activity depends on the amount of Pd loaded, and Pd_2/TiO_2 shows the highest activity. The H–Pd species are formed on the surface Pd atoms and, hence, the number of surface Pd atoms would strongly affect the denitrogenation activity. As shown in Figure 2-2, the high-resolution TEM images of catalysts revealed that the shape of Pd particles is a part of cuboctahedron surrounded by the (111) and (100) facets. The Pd particles on TiO_2 can therefore simply be modeled as a fcc cuboctahedron. This structure is generally used as a model for cubic fcc metal
nanoparticles. The numbers of surface metal atoms calculated based on this model are often employed for determination of active site in several catalytic systems such as hydrogenation of allyl alcohols with H₂ on Pd particles,²⁷ steam reforming of methane on Pt particles,²⁸ and oxidation of cinnamyl alcohols on Au particles.²⁹ The fcc cuboctahedron model therefore allows rough determination of the number of surface Pd atoms on the nanoparticles. Considering the full shell close packing cuboctahedron for Pd particle where one Pd atom is surrounded by twelve others, the number of total Pd atoms per Pd particle (N_{total}*) is expressed by eq. 5 using the number of shells (m). N_{total}* is rewritten with the average diameter of Pd particles (d_{Pd} / nm) and the atomic diameter of Pd (0.274 nm).³⁰ The number of surface Pd atoms per Pd particle (N_{surface}*) is expressed by eq. 6.

\[
N_{total}^* = \frac{10m^3 - 15m^2 + 11m - 3}{3} = \left( \frac{d_{Pd}}{1.105 \times 0.274} \right)^3
\] (5)

\[
N_{surface}^* = 10m^2 - 20m + 12
\] (6)

The number of Pd particles per gram catalyst (n_{particle}) is expressed by eq. 7, using the percent amount of Pd loaded on the catalyst \(\chi\) (wt%) = Pd/(Pd + TiO₂) × 100], molecular weight of Pd \(M_w = 106.42\) g mol⁻¹, and \(N_{total}^*\). The number of surface Pd atoms per gram catalyst \(N_{surface}^*\) is therefore expressed by eq. 8.

\[
n_{particle} (mol g^{-1}) = \frac{\chi}{100 \times M_w \times N_{total}^*}
\] (7)

\[
N_{surface} (mol g^{-1}) = N_{surface}^* \times n_{particle}
\] (8)

The \(N_{surface}^*\) values for respective Pdₓ/TiO₂ catalysts can therefore be calculated using their \(d_{Pd}\) values determined by the TEM observations (Figure 2-1). As shown by the open symbols in Figure 2-6, the \(N_{surface}^*\) values increase with an increase in the amount of Pd loaded; the values are 19.8 μmol g⁻¹ (Pd₀.₅/TiO₂), 27.8 (Pd₁/TiO₂), 45.5 (Pd₂/TiO₂), and 73.1 (Pd₄/TiO₂), respectively. To clarify the hydrodenitrogenation activity per surface Pd atoms, the turnover number for the reaction per surface Pd atoms on respective catalyst (TON_{surface}) was determined based on eq. 9, using the amount of toluene formed (mol) during the photocatalytic reaction of benzonitrile for 6 h in the presence of 10 mg catalyst (Table 2-2).

\[
TON_{surface} = \frac{[toluene formed]}{N_{surface} \times 10 \times 10^{-3}}
\] (9)

As shown by the black symbols in Figure 2-6, the TON_{surface} values for Pd₀.₅/TiO₂, Pd₁/TiO₂, and Pd₂/TiO₂ are almost the same. This suggests that these catalysts produce the surface H–Pd species with
similar efficiency. The higher activity of Pd₂/TiO₂ than Pd₆/TiO₂ and Pd₁/TiO₂ (Table 2-2) is therefore because larger number of surface H–Pd species is produced due to the larger number of surface Pd atoms (N_surface).

Figure 2-6. (Open symbol) The number of surface Pd atoms per gram Pdₓ/TiO₂ catalyst (N_surface), and (closed symbol) the turnover number for toluene formation per surface Pd atoms on respective catalysts during photocatalytic reaction of benzonitrile (TON_surface). Reaction conditions for benzonitrile were identical to those in Table 2-2.

Figure 2-7. Schematic representation of the Schottky barrier created at the Pd/TiO₂ heterojunction.
In contrast, the TON\textsubscript{surface} value of Pd\textsubscript{0}/TiO\textsubscript{2} is much lower than that of lower Pd loading catalysts (Figure 2-6), suggesting that the efficiency for H–Pd formation on the catalyst is lower. This is because the photocatalytic oxidation and reduction efficiency is decreased by the amount of Pd loaded. As shown in runs 2–5 (Table 2-2), the amounts of acetaldehyde and H\textsubscript{2} produced on Pd\textsubscript{0}/TiO\textsubscript{2} are much lower than those on lower Pd loading catalysts. It is well known that, as shown in Figure 2-7, the metal/semiconductor heterojunction creates a Schottky barrier ($\phi_0$), and the $\phi_0$ height increases with an increase in the amount of metal loaded.\textsuperscript{31} The increased $\phi_0$ height by the increased Pd loadings therefore suppresses smooth transfer of the conduction band e$^-$ to the Pd particles. This may result in inefficient charge separation between h$^+$ and e$^-$ and exhibit decreased photocatalytic activity. As a consequence, the H–Pd formation is suppressed, thus resulting in decreased denitrogenation activity. These findings indicate that the Pd\textsubscript{0}/TiO\textsubscript{2} catalyst, with relatively low $\phi_0$ height and large number of surface Pd atoms, exhibits the highest activity for photocatalytic hydrodenitrogenation of aromatic cyanides.

4. Conclusion

TiO\textsubscript{2} loaded with Pd particles (Pd/TiO\textsubscript{2}) were used as catalysts for photocatalytic hydrodenitrogenation of aromatic cyanide in ethanol as a hydrogen source. These catalysts, when irradiated by UV light at room temperature, promote denitrogenation and produce the corresponding toluene derivatives and triethylamine with very high selectivity. Photoexcited Pd/TiO\textsubscript{2} produces acetaldehyde and the active H–Pd species. Consecutive reactions involving hydrogenation by H–Pd species and condensation with aldehyde facilitate efficient hydrodenitrogenation. The amount of Pd loaded and the size of Pd particles strongly affect the denitrogenation activity. The Pd/TiO\textsubscript{2} catalyst with a relatively low Schottky barrier height at the Pd/TiO\textsubscript{2} heterojunction and a large number of surface Pd atoms is necessary for efficient denitrogenation.

5. References


Chapter III

N-Monoalkylation of Amines with Alcohols on TiO₂ Loaded with Pd Nanoparticles

1. Introduction

Tandem catalysis that enables multistep reactions in one pot has attracted a great deal of attention because it avoids the isolation of unstable intermediates and reduces the production of wastes.¹⁻³ A variety of one-pot synthetic procedures have been proposed, but many of these employ homogeneous catalysts, which generally suffer from product contamination and limited recyclability.⁴⁻⁶ Development of heterogeneous catalytic systems that promote efficient one-pot synthetic reactions is currently the focus of attention.⁷⁻¹¹

Secondary amines are one of the most important classes of chemicals that are widely used for synthesis of pharmaceuticals and agricultural chemicals.¹² Traditionally, these compounds are synthesized by N-monoalkylation of primary amines with alkyl halides.¹²⁻¹⁴ This method, however, requires stoichiometric or excess amount of inorganic bases, with a concomitant formation of large amounts of inorganic salts as waste.

An alternative environmentally-friendly way for secondary amine synthesis is the N-alkylation of primary amines with alcohols as the alkylating reagents in the presence of transition metal catalysts, so-called “borrowing hydrogen (H) strategy”.¹⁵⁻¹⁸ The reaction proceeds via three consecutive catalytic steps in one pot: (i) dehydrogenation of an alcohol initially proceeds, producing aldehyde and H atoms on the metal; (ii) catalytic condensation of the formed aldehyde with primary amine produces imine; and, (iii) the imine is hydrogenated by the H atoms, giving the secondary amine. Although many homogeneous catalysts such as Pt-, Ru-, and Ir-complexes, have been proposed so far,¹⁹⁻二十四 these methods have shortcomings in the recovery and reuse of expensive catalysts and/or the indispensable use of co-catalysts such as bases and stabilizing ligands. The design of easily recyclable heterogeneous catalytic systems is therefore desirable.

Several heterogeneous systems have also been proposed for one-pot secondary amine synthesis such as Pd oxides supported on Fe₂O₃,²⁵ Pd particles supported on boehmite nanofibers,²⁶ Ag clusters supported on Al₂O₃ (in the presence of FeCl₃·6H₂O as a homogeneous Lewis acid),²⁷ Ru or Cu hydroxide supported on Al₂O₃,²₈⁻₃¹ Au particles supported on TiO₂,³² and Pd particles supported on MgO.³³ All of these systems produce secondary amines selectively, but require relatively high reaction temperatures (>363 K).
The purpose of the present work is to design heterogeneous catalytic systems that promote \( N \)-monoalkylation of primary amines with alcohols at room temperature. It is well known that photoexcitation of semiconductor \( \text{TiO}_2 \) loaded with noble metal particles such as \( \text{Pt} \),\(^{34} \) \( \text{Ag} \),\(^{35} \) \( \text{Au} \),\(^{36} \) and \( \text{Pd} \)\(^{37} \) under inert gas atmosphere successfully promotes dehydrogenation of alcohols and produces aldehydes at room temperature. The removed \( H^+ \) are reduced by the photoformed electrons on the metal particles and are transformed to \( H \) atoms (\( H \)-metal species), which are finally removed from the metal surface by the formation of \( H_2 \).\(^{38} \) This indicates that \( \text{TiO}_2 \) loaded with metal particles, when photoactivated in alcohol, produces aldehyde and \( H \) atoms at room temperature. The formed aldehyde may react with primary amine on the Lewis acid site on the \( \text{TiO}_2 \) surface and produce imine.\(^{34,39} \) The imine may then be hydrogenated by the \( H \) atoms formed on the metal surface\(^{40} \) and converted to secondary amine.

Based on the above scenario, we studied the \( N \)-alkylation of primary amines with alcohols in the presence of metal-loaded \( \text{TiO}_2 \) under photoirradiation (\( \lambda > 300 \) nm). Here we report that \( \text{TiO}_2 \) loaded with \( \text{Pd} \) particles (\( \text{Pd}/\text{TiO}_2 \)) successfully promotes \( N \)-monoalkylation of primary amines at room temperature, via three consecutive steps involving (i) dehydrogenation of alcohols on the photoactivated \( \text{TiO}_2 \) surface; (ii) catalytic condensation of the formed aldehyde and amine; and, (iii) hydrogenation of the formed imine on the \( \text{Pd} \) surface. We found that the reaction efficiency strongly depends on the size of \( \text{Pd} \) particles. The catalyst loaded with 0.3 wt % \( \text{Pd} \), containing 2–2.5 nm \( \text{Pd} \) particles, shows the highest activity.

2. Experimental

2-1. Materials

All reagents were purchased from Wako, Tokyo Kasei, and Sigma-Aldrich and used without further purification. Japan Reference Catalyst JRC-TIO-4 \( \text{TiO}_2 \) particles were kindly supplied from Catalysis Society of Japan.

\( \text{Pd}/\text{TiO}_2 [x \text{ (wt\%)}] = 0.1, 0.3, 0.5, \) and 1.0] were prepared as follows: \( \text{TiO}_2 \) (1.0 g) and \( \text{Pd(NO}_3)_2 \) (2.2, 6.5, 10.9, or 21.9 mg) were added to water (40 mL) and evaporated under vigorous stirring at 353 K for 12 h. The obtained powders were calcined at 673 K under air flow (0.5 L min\(^{-1} \)) and then reduced at 673 K under \( H_2 \) flow (0.2 L min\(^{-1} \)). The heating rate and holding time at 673 K for these treatments were 2 K min\(^{-1} \) and 2 h, respectively. \( \text{Ag}/\text{TiO}_2 \) and \( \text{Pt}/\text{TiO}_2 \) were prepared in a similar manner to those for \( \text{Pd}/\text{TiO}_2 \), using \( \text{AgNO}_3 \) (4.7 mg) or \( \text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O} \) (8.0 mg) as precursor.

\( \text{Au}/\text{TiO}_2 \) was prepared by a deposition-precipitation method as follows: \( \text{HAuCl}_4\cdot\text{H}_2\text{O} \) (6.3 mg)
was added to water (50 mL). The pH of the solution was adjusted to 7 by an addition of 1 M NaOH. TiO₂ (1.0 g) was added to the solution and stirred vigorously at 353 K for 3 h. The solids were recovered by centrifugation and washed with water. The obtained solids were dried at 353 K and calcined at 673 K for 2 h under air flow (0.5 L min⁻¹).

2-2. Photoreaction

Each of the respective catalysts (10 mg) was suspended in alcohol (5 mL) containing required amount of amine within a Pyrex glass tube (ϕ10 mm; capacity, 20 mL). The tube was sealed with a rubber septum cap. The catalyst was dispersed by ultrasonication for 5 min, and N₂ was bubbled through the solution for 5 min. The tube was photoirradiated with magnetic stirring at 298 K by a 2 kW Xe lamp (λ >300 nm; Ushio Inc.). The light intensity at 300–400 nm is 18.2 W m⁻². After photoirradiation, the gas-phase product was analyzed by GC-TCD (Shimadzu; GC-8A). The resulting solution was recovered by centrifugation and analyzed by GC-FID (Shimadzu; GC-1700), where the substrate and product concentrations were determined with authentic samples. Identification of the products was performed by Shimadzu GC-MS system (GCMS-QP5050A).

2-3. Hydrogenation by H₂

Each of the respective catalysts was suspended in solution (5 mL) containing substrate within a Schlenk tube. The catalyst was dispersed by ultrasonication for 5 min, and H₂ was bubbled through the solution for 5 min, where the H₂ pressure was maintained at 1 atm using a balloon. The tube was placed on the digitally-controlled water bath with magnetic stirring at 298 K.

2-4. Analysis

Total Pd amounts of the catalysts were determined by an X-ray fluorescence spectrometer (Seiko Instruments, Inc.; SEA2110). Diffuse reflectance UV-vis spectra were measured on an UV-vis spectrophotometer (Jasco Corp.; V-550 with Integrated Sphere Apparatus ISV-469) with BaSO₄ as a reference.⁵⁹,⁶⁰ TEM observations were carried out using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV.⁶¹ The cuboctahedron Pd particles were created on the Crystal Studio Ver. 9.0 software (CrystalSof. Inc) and used for calculation of the number of Pd atoms.⁵⁹ Ab initio calculations were carried out with the Gaussian 03 program, and the geometry optimization was performed with the density functional theory (DFT) using the B3LYP function with the 6–31G* basis set.⁶²,⁶³
3. Results and discussion

3-1. Catalytic activity of metal-loaded TiO₂

Table 3-1. Catalyst properties and the results for N-alkylation of aniline with benzyl alcohol on various catalysts under photoirradiation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>(d_{pd} / \text{nm}^a)</th>
<th>Aniline conv. / % (^b)</th>
<th>Yields / % (^b, c)</th>
<th>Amount of product formed / (\mu\text{mol}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
<td>Benzaldehyde</td>
</tr>
<tr>
<td>1</td>
<td>TiO₂</td>
<td>11</td>
<td>10</td>
<td>0</td>
<td>&lt;1</td>
</tr>
<tr>
<td>2</td>
<td>Au₀.₃/TiO₂</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>Ag₀.₃/TiO₂</td>
<td>9</td>
<td>6</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>Pt₀.₃/TiO₂</td>
<td>56</td>
<td>53</td>
<td>3</td>
<td>84</td>
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<tr>
<td>5</td>
<td>Pd₀.₃/TiO₂</td>
<td>1.6</td>
<td>65</td>
<td>8</td>
<td>49</td>
</tr>
<tr>
<td>6</td>
<td>Pd₀.₃/TiO₂</td>
<td>2.3</td>
<td>&gt;99</td>
<td>6</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td>Pd₀.₃/TiO₂</td>
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<td>91</td>
<td>9</td>
<td>81</td>
</tr>
<tr>
<td>8</td>
<td>Pd₁₁.₀/TiO₂</td>
<td>4.1</td>
<td>89</td>
<td>19</td>
<td>64</td>
</tr>
<tr>
<td>9(^d)</td>
<td>Pd₀.₃/TiO₂</td>
<td>&gt;99</td>
<td>7</td>
<td>92</td>
<td>7</td>
</tr>
</tbody>
</table>

\(^a\) Average diameter of Pd particles determined by TEM observations (Figure 1). \(^b\) Determined by GC. \(^c\) \(d = [\text{product formed}] / [\text{initial amount of aniline}] \times 100. \(^d\) The result obtained by the reuse of catalyst (entry 6) after simple washing with ethanol.

The catalytic activity of metal-loaded TiO₂, \(M_x/\text{TiO}_2 \ [x (\text{wt} \%) = M/(M + \text{TiO}_2) \times 100\], was studied for \(N\)-alkylation of primary amine with alcohol. The catalysts loaded with 0.3 wt % metal particles such as Au, Pt, Ag, and Pd were prepared with JRC-TIO-4 TiO₂ supplied from the Catalyst Society of Japan (equivalent to Degussa P25; anatase/rutile = ca. 80/20; average particle size, 24 nm; BET surface area, 59 m² g⁻¹). Metal loadings were carried out by the deposition-precipitation method\(^4\) for Au and by the impregnation-reduction method\(^34\) for Pt, Ag, and Pd, respectively. These catalysts were used for \(N\)-alkylation of aniline with benzyl alcohol. The reactions were carried out by photoirradiation (\(\lambda >300 \text{ nm}, 6 \text{ h}\) of a benzyl alcohol solution (5 mL) containing aniline (50 \(\mu\text{mol}\)) with respective catalyst (10 mg) at room temperature under \(\text{N}_2\) atmosphere (1 atm). The conversion of aniline and the yield of N-benzylidenaniline (1) and N-benzylphenylamine (2) (= [product formed] / [initial amount of aniline] \(\times\)
100) are summarized in Table 3-1. With bare TiO₂ (entry 1), the aniline conversion is only 11% and the imine (N-benzylidenedianiline: 1) is formed as the main product, where the secondary amine (N-benzylphenylamine: 2) is scarcely produced. Au₀.₃/TiO₂ and Ag₀.₃/TiO₂ catalysts are also ineffective (entries 2 and 3); their aniline conversions are <10%. In these cases, the amount of benzaldehyde formed is significantly low (<20 μmol). This implies that photocatalytic oxidation of alcohol does not occur efficiently on these catalysts and does not provide enough amount of aldehyde for condensation with aniline. As shown in entry 4, Pt₀.₃/TiO₂ shows relatively high aniline conversion (56%). The 2 yield is however only 3%, and imine (1) is produced mainly. This indicates that hydrogenation of imine does not occur efficiently on the Pt₀.₃/TiO₂ catalyst. In contrast, Pd₀.₃/TiO₂ (entry 6) produces 2 with almost quantitative yield (92%). The results clearly indicate that Pd/TiO₂ catalyst is highly active for N-monoalkylation.

3-2. Catalytic activity of Pd/TiO₂

Pdₓ/TiO₂ catalysts with different Pd loadings (x = 0.1, 0.3, 0.5, and 1.0 wt %) were prepared to clarify their activity. Figure 3-1 shows the typical transmission electron microscopy (TEM) images of Pd₀.₃/TiO₂. Highly dispersed Pd nanoparticles were observed for all of the Pdₓ/TiO₂ catalysts. As shown in Figure 3-1, the size of Pd particles (dₚ) determined by the TEM observations increases with an increase in the Pd loadings; the average diameters for x = 0.1, 0.3, 0.5, and 1.0 catalysts are 1.6, 2.3, 2.6, and 4.1 nm, respectively. In addition, high-resolution TEM image of catalyst (Figure 3-2) revealed that the Pd particles can be indexed as fcc structure, as well as bulk Pd metal (JCPDS 46-1043). Figure 3-3 shows the diffuse reflectance UV-vis spectra of respective catalysts. The catalysts with higher Pd loadings show increased absorbance at λ >300 nm due to the light scattering by the Pd particles.
Figure 3-1. Typical TEM image of Pd$_{0.3}$/TiO$_2$ catalyst, and the size distributions of Pd particles on the respective Pd$_x$/TiO$_2$ catalysts.
Figure 3-2. High-resolution TEM images of Pd$_{0.5}$/TiO$_2$. (a) The incident beam direction is [0, -1, 1]. (b) This particle is twinned particle. The incident beam directions are [0, -1, 1] and [0, 1, -1].
Table 3-1 (entries 5–8) summarizes the results for N-alkylation of aniline with benzyl alcohol in the presence of Pd/TiO₂ catalysts. Among the catalysts, Pd₀.₃/TiO₂ (entry 6) shows the highest aniline conversion (>99%) and the highest 2 yield (92%). The catalysts with lower or higher Pd loadings show decreased activity. These data suggest that Pd₀.₃/TiO₂ shows the best catalytic activity, and the activity strongly depends on the amount of Pd loaded. It is noted that the Pd₀.₃/TiO₂ catalyst is reusable for further reaction. As shown in Table 3-1 (entry 9), Pd₀.₃/TiO₂, when reused for reaction after simple washing with ethanol, shows the aniline conversions and 2 yield similar to that obtained with the virgin catalyst (entry 6). This indicates that the catalyst is reusable without the loss of activity and selectivity. In addition, Pd₀.₃/TiO₂ is applicable for synthesis of several kinds of secondary amines. As shown in Table 3-2, photoirradiation of Pd₀.₃/TiO₂ in alkyl or benzyl alcohols containing several kinds of primary amines produces the corresponding secondary amines with very high yields (>82%).
Table 3-2. \(N\)-alkylation of various amines with alcohols on the Pd\(_{0.5}\)/TiO\(_2\) catalyst under photoirradiation.\(^{a}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohol</th>
<th>Amine</th>
<th>(t)/h</th>
<th>Amine conv. /%(^b)</th>
<th>Product</th>
<th>Yield /%(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>(\text{NH}_2)</td>
<td>6</td>
<td>&gt;99</td>
<td>[Image]</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>(\text{NH}_2)</td>
<td>12</td>
<td>&gt;99</td>
<td>[Image]</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>(\text{NH}_2)</td>
<td>14</td>
<td>98</td>
<td>[Image]</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>(\text{OH})</td>
<td>(\text{NH}_2)</td>
<td>12</td>
<td>&gt;99</td>
<td>[Image]</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>(\text{OH})</td>
<td>16</td>
<td>94</td>
<td>[Image]</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>(\text{NH}_2)</td>
<td>12</td>
<td>&gt;99</td>
<td>[Image]</td>
<td>95</td>
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<tr>
<td>7</td>
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<td>(\text{NH}_2)</td>
<td>12</td>
<td>&gt;99</td>
<td>[Image]</td>
<td>82</td>
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<tr>
<td>8</td>
<td>(\text{OH})</td>
<td>(\text{NH}_2)</td>
<td>3</td>
<td>&gt;99</td>
<td>[Image]</td>
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</tr>
<tr>
<td>9</td>
<td>(\text{OH})</td>
<td>(\text{NH}_2)</td>
<td>4</td>
<td>&gt;99</td>
<td>[Image]</td>
<td>91</td>
</tr>
</tbody>
</table>

\(^{a}\) Reaction conditions: alcohol, 5 mL; amine, 50 \(\mu\)mol; catalyst, 10 mg; temperature, 298 K; \(N_2\), 1 atm; \(\lambda\) >300 nm; \(^{b}\) Determined by GCs.

3-3. Mechanism for \(N\)-alkylation

The Pd/TiO\(_2\) catalysts promote \(N\)-alkylation of amine with alcohol via tandem photocatalytic and catalytic reactions. The reactions are initiated by photoexcitation of TiO\(_2\), producing the electron (\(e^-\)) and positive hole (\(h^+\)) pairs.

\[
\text{TiO}_2 + \hbar \nu \rightarrow h^+ + e^- \quad (1)
\]

The \(h^+\) oxidizes alcohol and produces aldehyde and \(H^+\).

\[
R_1-\text{CH}_2\text{OH} + 2h^+ \rightarrow R_1-\text{CHO} + 2H^+ \quad (2)
\]

\(H^+\) is reduced on the surface of Pd particles by the \(e^-\) transferred from the TiO\(_2\) conduction band, and transformed to the surface H atom (H–Pd species).

\[
H^+ + e^- + \text{Pd} \rightarrow \text{H–Pd} \quad (3)
\]

Parts of the H atoms are removed from the surface of Pd particles as \(H_2\) gas by coalescence.

\[
\text{H–Pd} + \text{H–Pd} \rightarrow H_2^\uparrow + 2\text{Pd} \quad (4)
\]

Condensation of the formed aldehyde with primary amine by the Lewis acid site on the TiO\(_2\) surface produces the imine. The reaction occurs reversibly as follows:\(^{34,39}\)
The imine is hydrogenated by the H–Pd species and is transformed to secondary amine.\textsuperscript{40}

\[
R_1-\text{CHO} + R_2-\text{NH}_2 \xrightarrow{\text{Hd}} R_1-\text{CH}==\text{N}==\text{R}_2 + \text{H}_2\text{O} \tag{5}
\]

\[
R_1-\text{CH}==\text{N}==\text{R}_2 + 2\text{H}--\text{Pd} \rightarrow R_1-\text{CH}_2==\text{NH}==\text{R}_2 + 2\text{Pd} \tag{6}
\]

**Figure 3-4** shows the time-dependent change in the amounts of substrate and products during photocatalytic reaction of aniline with benzyl alcohol in the presence of Pd\textsubscript{0.1}/TiO\textsubscript{2}, Pd\textsubscript{0.3}/TiO\textsubscript{2}, and Pd\textsubscript{1.0}/TiO\textsubscript{2} catalysts, respectively. As shown in **Figure 3-4b**, photoirradiation of Pd\textsubscript{0.3}/TiO\textsubscript{2} produces benzaldehyde and H\textsubscript{2} at the initial stage. Then, the amount of aniline decreases, and the imine 1 and secondary amine 2 appear. The amount of 1 stays very low and the amount of 2 increases with time; 6 h photoirradiation leads to almost quantitative transformation of aniline to 2. These substrate and product profiles suggest that the above reaction sequence (eqs 1–6) proceeds efficiently on the Pd\textsubscript{0.3}/TiO\textsubscript{2} catalyst. In contrast, with Pd\textsubscript{0.1}/TiO\textsubscript{2} and Pd\textsubscript{1.0}/TiO\textsubscript{2} (**Figure 3-4a** and **c**), the formation of 2 is much slower than that obtained with Pd\textsubscript{0.3}/TiO\textsubscript{2}; quantitative formation of 2 requires more than 10 h. These data suggest that Pd\textsubscript{0.3}/TiO\textsubscript{2} shows the highest activity for N-alkylation, and the amount of Pd loaded strongly affects the catalytic activity.

**Figure 3-4.** Time-dependent change in the amounts of substrate and products during photoreaction of benzyl alcohol and aniline with (a) Pd\textsubscript{0.1}/TiO\textsubscript{2}, (b) Pd\textsubscript{0.3}/TiO\textsubscript{2}, and (c) Pd\textsubscript{1.0}/TiO\textsubscript{2} catalysts. Reaction conditions are identical to those in Table 1.

**3-4. Effect of Pd amount on the reaction steps**

The effects of Pd amount on the respective reaction steps (eqs. 2–6) for N-alkylation were studied to clarify the reason for high activity of Pd\textsubscript{0.3}/TiO\textsubscript{2}. The oxidation of alcohol by the photoformed h\textsuperscript{+} (eq. 2) as the first step for reaction was studied by photoirradiation of respective catalysts (10 mg) in benzyl
alcohol (5 mL) without aniline. Figure 3-5 (white) shows the amount of benzaldehyde formed by 6 h photoirradiation. Pd$_{0.1}$/TiO$_2$ produces the highest amount of aldehyde and the amount decreases with the Pd loadings. This suggests that lower Pd loading catalysts are more active for photocatalytic oxidation of alcohol. It is well known that a metal/semiconductor heterojunction creates a Schottky barrier. Photoformed conduction band e^- of semiconductor overcomes this barrier and is trapped by metal particles, resulting in enhanced charge separation between h^+ and e^- . The charge separation efficiency therefore strongly depends on the height of Schottky barrier. The increased metal loadings onto semiconductor load to an increase in the height of Schottky barrier due to the electron transfer from semiconductor to metal. The increased barrier height by large Pd loadings probably suppresses the migration of conduction band e^- to Pd particles. This may decrease the charge separation efficiency and result in decreased photocatalytic aldehyde formation (Figure 3-5). However, as shown in Table 3-1 (entries 5–8), all of the Pd$_x$/TiO$_2$ catalysts produce benzaldehyde with amounts larger than that of aniline (50 µmol). This suggests that enough amount of aldehyde for condensation with aniline is produced on all of the catalysts, and the photocatalytic alcohol oxidation is not the rate-determining step for N-alkylation.

Figure 3-5. Amount of products formed during photoreaction of benzyl alcohol with respective catalysts in the absence of amine.

Condensation of amine with aldehyde (eq. 5) is the next step for N-alkylation. The reaction is catalyzed by Lewis acid site on the TiO$_2$ surface$^{34,39}$ and is not affected by the amount of Pd loaded. Table 3-3 summarizes the results for condensation between aniline and 2 equiv of benzaldehyde in the
presence of respective catalysts for 3 h at 298 K in the dark. The absence of catalyst (entry 1) produces 1 with only 29% yield. In contrast, addition of bare TiO$_2$ (entry 2) produces 1 with >90% yield. The yield of 1 scarcely changes by the catalysts with different Pd loadings (entries 3–6). These data clearly suggest that the imine formation (eq. 5) is also not the rate-determining step for N-alkylation.

**Table 3-3.** Condensation of benzaldehyde with aniline on the respective catalysts in the dark.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>1 yield [%]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>TiO$_2$</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>Pd$_{0.1}$/TiO$_2$</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>Pd$_{0.3}$/TiO$_2$</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>Pd$_{0.5}$/TiO$_2$</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>Pd$_{1.0}$/TiO$_2$</td>
<td>95</td>
</tr>
</tbody>
</table>

$^a$ Determined by GC.

As a result of the above, the rate-determining step for N-alkylation is the hydrogenation of imine by the H atom formed on the surface of Pd particles (eq. 6) as the final step for reaction sequence. The imine hydrogenation is strongly affected by the size of Pd particles loaded. This is confirmed by hydrogenation of imine 1 with molecular hydrogen (H$_2$) as a hydrogen source. The reaction was performed in MeCN containing 1 with H$_2$ (1 atm) in the presence of respective Pd$_x$/TiO$_2$ catalysts at the constant Pd amount (0.28 µmol) for 2 h in the dark. Figure 3-6 (black) shows the relationship between the diameter of Pd particles ($d_{pd}$) and the yield of secondary amine (2) formed. Smaller Pd particles have larger surface area and possess larger number of surface Pd atoms. The 2 yields, however, increase with an increase in the size of Pd particles. This indicates that all of the surface Pd atoms are not the active site, and the Pd atoms on the specific surface site behave as the active site for imine hydrogenation.
Figure 3-6. The yields of secondary amine 2 obtained during hydrogenation of imine 1 in MeCN or benzyl alcohol with respective Pd/TiO₂ catalysts (Pd: 0.28 μmol) under H₂ in the dark condition. The amounts of catalysts used are: 30 mg (Pd₀.₁), 10 mg (Pd₀.₃), 5 mg (Pd₀.₅), and 3 mg (Pd₁), respectively.

3-5. Active site for imine hydrogenation

Specific active site for imine hydrogenation on the Pd particles must be identified. Morphology and size of metal particles strongly affect the catalytic activity due to the electronic and geometric effects. Metal particles contain different types of surface atoms located at the vertex, edge, square, and triangle sites. The number of these atoms changes substantially with the size of particles. As shown in Figure 3-2, high-resolution TEM images of catalysts revealed that the shape of Pd particle is part of cuboctahedron, which is surrounded by [111] and [100] surfaces. The Pd particles on TiO₂ surface can therefore simply be modeled as a fcc cuboctahedron, as shown in Figure 3-7a, which is often used for related nanoparticle systems. This allows rough determination of the number of Pd atoms on the respective surface sites. Considering the full shell close packing cuboctahedron for Pd particle where one Pd atom is surrounded by twelve others, the number of total Pd atoms per particle (Nₜₐ₅*) and the number of surface Pd atoms per particle (Nₚₙₐ₅*) can be expressed by the following equations using the shell number (m).
Figure 7. (a) The fcc cuboctahedron model for Pd particles. (b) The largest cross-sectional (111) hexagonal facet of the Pd particle. (c) The unit lattice of Pd particle.

\[ N_{\text{total} \ast} = \frac{1}{3} (2m-1)(5m^2 - 5m + 3) \]  \hspace{1cm} (7)

\[ N_{\text{surface} \ast} = 10m^2 - 20m + 12 \]

\[ = N_{\text{vertex} \ast} + N_{\text{edge} \ast} + N_{\text{square} \ast} + N_{\text{triangle} \ast} \]  \hspace{1cm} (8)

The numbers of Pd atoms on the specific surface sites \( (N_{\text{specific} \ast}) \) such as vertex, edge, square, and triangle sites per Pd particles are therefore expressed by the following equations.\(^5^1\)

\[ N_{\text{vertex} \ast} = 12 \]  \hspace{1cm} (9)

\[ N_{\text{edge} \ast} = 24(m-2) \]  \hspace{1cm} (10)

\[ N_{\text{square} \ast} = 6(m-2)^2 \]  \hspace{1cm} (11)

\[ N_{\text{triangle} \ast} = 4(m-3)(m-2) \]  \hspace{1cm} (12)

As shown in Figure 3-7b, the number of Pd atoms on the diagonal line of the largest cross-sectional (111) facet of Pd particle is expressed as \( 2m-1 \). The lattice constant of Pd is 0.389 nm (Figure 3-7c),\(^5^2\) and the atomic diameter of Pd is 0.274 nm.\(^5^3\) The diameter of Pd particle \( (d_{\text{pd}}) \) is therefore expressed as follows.

\[ d_{\text{pd}} \text{ (nm)} = \frac{0.389}{\sqrt{2}} \{ (2m-1) - 1 \} + 0.274 \]  \hspace{1cm} (13)

The number of Pd particles per unit weight of Pd \( (n_{\text{particle}}) \), and the number of Pd atoms on the specific surface site (vertex, edge, square, triangle) per unit weight of Pd \( (N_{\text{specific}}) \) can therefore be expressed
using the molecular weight of Pd \[M_w (= 106.42 \text{ g mol}^{-1})\], as follows.

\[
n_{\text{particle}} (\text{mol g}^{-1}) = \frac{1}{M_w \times N_{\text{total}}} \tag{14}
\]

\[
N_{\text{specific}} (\text{mol g}^{-1}) = N_{\text{specific}} \times n_{\text{particle}} \tag{15}
\]

As shown in Figure 3-1, the average diameters of Pd particles \(d_{\text{Pd}}\) for catalysts were determined by TEM observations to be 1.6 nm (Pd0.1/TiO2), 2.3 nm (Pd0.3/TiO2), 2.6 nm (Pd0.5/TiO2), and 4.1 nm (Pd1.0/TiO2), respectively. The shell numbers \(m\) for Pd particles on the respective catalysts can therefore be calculated using eq 13. The numbers of Pd atoms on the specific surface site per unit weight of Pd \(N_{\text{specific}}\) can then be determined using eqs 9–12, 14, and 15. Figure 3-8 shows the relationship between the diameter of Pd particles and their respective \(N_{\text{specific}}\) values. The \(N_{\text{vertex}}\) and \(N_{\text{edge}}\) values decrease with an increase in the size of Pd particle, and the \(N_{\text{square}}\) values scarcely change with the Pd particle size. These profiles are completely different from the catalytic activity of Pd particles for imine hydrogenation (Figure 6, black). In contrast, the \(N_{\text{triangle}}\) value increases with an increase in the Pd particle size, and the profile is very similar to the imine hydrogenation profile. This calculation result implies that Pd atoms on the triangle site are active for imine hydrogenation.

\[
\begin{align*}
&\text{triangle} & \text{vertex} & \text{square} & \text{edge} \\
&\text{Pd}_{0.1} & \text{Pd}_{0.3} & \text{Pd}_{0.5} & \text{Pd}_{1.0} \\
&0 & 5 & 0 & 0 \\
&0 & 3 & 3 & 3 \\
&1 & 2 & 3 & 4 \\
&d_{\text{Pd}} / \text{nm} & N_{\text{specific}} / \text{mmol g}^{-1} & N_{\text{specific}} / \text{mmol g}^{-1} & N_{\text{specific}} / \text{mmol g}^{-1}
\end{align*}
\]

Figure 3-8. Relationship between the diameter of Pd particles on the respective Pd/TiO2 catalyst and the number of Pd atoms on the specific surface site of Pd particle per unit weight of Pd.

This is further confirmed by the turnover number for imine hydrogenation per number of Pd atoms on the specific surface site (TON\(_{\text{specific}}\)). The amount of secondary amine 2 (mol) formed during hydrogenation of imine 1 by H\(_2\) with respective Pd/TiO2 catalysts in the dark (Figure 3-6) was divided
by the Pd amount (0.28 μmol) and the respective $N_{\text{specific}}$ values, using the following equation.

$$\text{TON}_{\text{specific}} = \frac{\text{[amount of product formed]}}{N_{\text{specific}} \times (0.28 \times 10^{-6})}$$ (16)

Figure 3-9 shows the relationship between the size of Pd particle on the catalysts and respective TON$^{\text{specific}}$ values. The TON$^{\text{vertex}}$, TON$^{\text{edge}}$, and TON$^{\text{square}}$ values change with the Pd particle size. In contrast, the TON$^{\text{triangle}}$ values for the respective catalysts are similar and are independent of the Pd particle size. This result clearly indicates that the Pd atoms on the triangle site are the active site for imine hydrogenation.

Figure 3-9. Relationship between the Pd particle size and the turnover number for hydrogenation of imine 1 per number of Pd atoms on the specific surface site (TON$^{\text{specific}}$). The TON$^{\text{specific}}$ value was calculated with the results for imine hydrogenation (Figure 6, black) using eq. 16.

The H atoms formed on the Pd particles diffuse around the particle surface, meaning that the H atoms exist randomly on all parts of the Pd particle surface. The strong dependence of the imine hydrogenation activity on the number of Pd atoms on the triangle site is probably due to the adsorption of imine onto the triangle site. The Pd atoms on the triangle site have higher coordination number (9) than those on the other surface sites such as vertex (5), edge (7), and square (8), and are charged more positively. The imine is therefore preferentially adsorbed onto the positively charged triangle site via $\pi$ electronic interaction with the aromatic ring and C=N bond. This adsorption may promote efficient hydrogenation by the H–Pd species, and result in clear relationship between the imine hydrogenation
activity and the number of Pd atoms on the triangle site. In the hydrogenation of alkyne and diene such as 2-methyl-3-butyne-2-ol and 1,3-butadiene on Pd particle catalysts with H₂, the catalytic activity also depends on the number of Pd atoms on the triangle site, and the dependence is also considered to be due to the adsorption of these olefins onto the positively charged triangle site. These reports support the above mechanism for imine hydrogenation.

3-6. Effect of alcohol on the imine hydrogenation

The above results suggest that the triangle site of Pd particles is the active site for imine hydrogenation. The number of these Pd atoms increases with an increase in the Pd particle size, and the Pdₓ/TiO₂ catalyst with higher Pd loadings, which contain larger Pd particles, efficiently promotes imine hydrogenation. However, as shown in Figure 3-4b and c, photocatalytic reaction of benzyl alcohol and aniline with Pdₓ/TiO₂ shows much lower activity for imine hydrogenation than Pd₀.₃/TiO₂. This is inconsistent with the results for imine hydrogenation with H₂ (Figure 3-6, black).

The lower imine hydrogenation activity of larger Pd particles is because alcohols are adsorbed onto the larger triangle site more strongly than imines and undergo hydrogenation. Figure 3-6 (white) shows the results for imine hydrogenation with H₂, when carried out in benzyl alcohol. The hydrogenation activity of smaller Pd particles is similar to that obtained in MeCN (black), but the activity of larger Pd particles is decreased significantly. This data clearly indicates that the imine hydrogenation on larger Pd particles is suppressed by alcohol. In these cases, GC analysis detected the formation of toluene. This indicates that, as reported, Pd particles promote hydrogenation of alcohol by the H–Pd species leading to hydrogenolysis.

Figure 3-10a shows the amount of toluene formed during hydrogenation of benzyl alcohol with H₂ in the dark with respective Pdₓ/TiO₂ catalysts at the identical Pd amount (0.28 μmol). The hydrogenation activity increases with the Pd particle size, and the profile is very similar to the imine hydrogenation profile (Figure 3-6, black). Figure 3-10b shows the turnover number for toluene formation per number of specific surface site (TON_specific) calculated using eq. 16. The TON_triangle values for all of the catalysts are similar as is the case for imine hydrogenation (Figure 3-9). These findings indicate that the hydrogenation of alcohol is also promoted on the triangle site of Pd particles, and this suppresses the imine hydrogenation.
Figure 3-10. (a) Amount of toluene formed during reaction of benzyl alcohol with respective Pd/TiO₂ catalysts (Pd: 0.28 μmol) under H₂ in the dark. The amounts of catalysts used are: 30 mg (Pdₐ₁), 10 mg (Pdₐ₂), 5 mg (Pdₐ₃), and 3 mg (Pd₁), respectively. (b) Relationship between the Pd particle size and the turnover number for toluene formation per number of Pd atoms on the specific surface site (TONspecific). The TONspecific values were calculated using eq. 16.

The strongly suppressed imine hydrogenation on larger Pd particles is probably due to the stronger adsorption of alcohol than imine onto larger triangle site by their different adsorption modes. As shown in Figure 3-11, benzyl alcohol has a planer structure and is adsorbed very strongly onto the Pd surface via π interaction of aromatic ring and the lone pair electron of oxygen atom. In contrast, the imine has a twisted structure and may be adsorbed more weakly onto the Pd surface. The interaction between
alcohol and the Pd surface is probably strengthened by an increase in the area of triangle site. This probably leads to enhanced alcohol adsorption onto the larger Pd particles and suppresses imine hydrogenation more strongly. As shown in Figures 3-4 and 5, larger amount of toluene is produced during photocatalytic reaction of alcohol in the presence of catalysts with larger Pd particle. This indicates that the decreased imine hydrogenation activity of larger Pd particle is due to the strong adsorption of alcohols. These results suggest that the Pd$_{0.5}$TiO$_2$ catalyst with 2–2.5 nm Pd particles, which contains relatively larger number of triangle site Pd atoms but does not allow strong adsorption of alcohols, shows the highest activity for imine hydrogenation and promotes efficient N-monoalkylation of primary amine with alcohol under photoirradiation.

![Figure 3-11](image)

Figure 3-11. Schematic representation of different adsorption modes of benzyl alcohol and imine 1 onto the surface of Pd particle. Geometry optimizations of the molecules were performed with B3LYP/6-31G* basis set.

4. Conclusion

We found that Pd/TiO$_2$ catalyst promotes N-monoalkylation of primary amine with alcohol under photoirradiation at room temperature. Several kinds of secondary amines are successfully produced with high yields. Tandem photocatalytic and catalytic reactions promote three consecutive reactions, consisting of Pd-assisted alcohol oxidation on the photoactivated TiO$_2$, catalytic condensation of the formed aldehydes with amines on the TiO$_2$ surface, and hydrogenation of formed imine with H atoms on the Pd particles. The rate-determining reaction is the imine hydrogenation as the final step. The reaction is promoted on the Pd atoms on the triangle site of the Pd particle via an adsorption of imine. The imine adsorption onto the larger triangle site is strongly suppressed by competitive adsorption of alcohol. As a result of this, the catalyst with 2–2.5 nm Pd particles, which contain relatively larger number of triangular Pd atoms and do not promote strong alcohol adsorption, shows the highest activity for imine
hydrogenation and promotes efficient N-alkylation of amine with alcohol under photoirradiation. This tandem catalytic system offers significant advantages: (i) no harmful byproduct forms; (ii) the reaction proceeds at room temperature; and, (iii) several secondary amines are successfully produced. The tandem reactions promoted by photocatalytic and catalytic actions, therefore, have a potential to be a powerful method for one-pot synthesis of organic compounds in an environmentally-friendly way.

5. References


Chapter IV

Dehalogenation of Organic Halides on TiO₂ Loaded with Bimetallic Pd-Pt Alloy Nanoparticles

1. Introduction

The dehalogenation of organic halides is a significant process for the removal of halogenated organic pollutants and the synthesis of fine chemicals. The reaction is currently carried out via the hydrodehalogenation processes with catalysts containing Pd particles using molecular hydrogen (H₂) as the hydrogen source, which inevitably holds explosion risks. Alternative methods with safe hydrogen sources such as alcohols are therefore desirable.

Recently, a H₂-free dehalogenation method with alcohol as the hydrogen source was proposed by Fuku et al. They employed a photocatalytic reaction using TiO₂ loaded with 1 wt% Pd particles (Pd/TiO₂). Photoirradiation (λ >300 nm) of a 2-PrOH solution containing chlorobenzene with Pd/TiO₂ and a base (NaOH) produces the corresponding benzene quantitatively. The reactions are initiated by photoexcitation of TiO₂, producing the electron (e⁻) and positive hole (h⁺) pairs (eqn (1)). The h⁺ oxidizes 2-PrOH and produces acetone and protons (eqn (2)). The H⁺ is activated by the reduction with e⁻ on the Pd particles (eqn (3)), and the formed hydrides species (H⁻–Pd) promote dehalogenation (eqn (4)). The removed Cl⁻ is solidified as NaCl by the reaction with NaOH (eqn (5)). The overall reaction is expressed as eqn (6).

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow \text{h}^+ + \text{e}^- \quad (1) \\
(\text{CH}_3)_2\text{CHOH} + 2\text{h}^+ & \rightarrow (\text{CH}_3)_2\text{CO} + 2\text{H}^+ \quad (2) \\
\text{H}^+ + 2\text{e}^- + \text{Pd} & \rightarrow \text{H}^-\text{–Pd} \quad (3) \\
\text{Ar}^-\text{C} + \text{H}^-\text–\text{Pd} & \rightarrow \text{Ar}^-\text{–H} + \text{Cl}^- + \text{Pd} \quad (4) \\
\text{H}^+ + \text{Cl}^- + \text{NaOH} & \rightarrow \text{H}_2\text{O} + \text{NaCl} \downarrow \quad (5) \\
\text{Ar}^-\text{Cl} + (\text{CH}_3)_2\text{CHOH} + \text{NaOH} & \rightarrow \text{Ar}^-\text{–H} + (\text{CH}_3)_2\text{CO} + \text{H}_2\text{O} + \text{NaCl} \downarrow \quad (6)
\end{align*}
\]

These reactions proceed at room temperature with alcohol as the hydrogen source, and have a potential to be a safe and sustainable dehalogenation process. The reactions, however, proceed very slowly when compared to the conventional method with H₂. The activity improvement is therefore necessary.

Herein, we report that TiO₂ loaded with bimetallic Pd-Pt alloy particles (PdPt/TiO₂) promotes highly efficient photocatalytic dehalogenation. The activity is more than three times that of Pd/TiO₂ and
higher than the conventional method with \( \text{H}_2 \). The high activity is due to the enhanced consumption of photoformed \( \text{e}^- \) on the Pt site by \( \text{H}^+ \) reduction and efficient transfer of the formed hydrogen atom to the adjacent Pd site within the alloy particles.

2. Experimental

2-1. Materials

All reagents were purchased from Wako, Tokyo Kasei, and Sigma-Aldrich and used without further purification. Japan Reference Catalyst JRC-TIO-4 TiO\textsubscript{2} particles were kindly supplied from Catalysis Society of Japan.

Pd\textsubscript{1}\text{Pt}/TiO\textsubscript{2} catalysts \([y \text{ wt\%} = \text{Pt/(Pt + TiO}_2) \times 100; y = 1, 3, 5, 7, 10]\) were prepared as follows: TiO\textsubscript{2} (0.5 g), Pd(NO\textsubscript{3})\textsubscript{2} (11 mg), and H\textsubscript{2}PtCl\textsubscript{6} (13, 27, 70, 94, 147 mg) were added to water and evaporated with vigorous stirring at 353 K for 12 h. The obtained powders were calcined at 673 K for 3 h under air flow and then reduced under H\textsubscript{2} at 473 K for 2 h.

Pd\textsubscript{1}+Pd\textsubscript{5}/TiO\textsubscript{2} catalyst was prepared as follows: TiO\textsubscript{2} (0.5 g) and Pd(NO\textsubscript{3})\textsubscript{2} (11 mg) were added to water and evaporated with vigorous stirring at 353 K for 12 h. The obtained powders were calcined at 673 K for 3 h under air flow and then reduced under H\textsubscript{2} at 473 K for 2 h. The obtained powders and H\textsubscript{2}PtCl\textsubscript{6} (70 mg) were added to water and evaporated at 353 K for 12 h under vigorous stirring. The resultant was calcined at 673 K for 3 h under air flow and reduced under H\textsubscript{2} at 473 K for 2 h.

2-2. Photoreaction procedure

Photoreactions were performed within a Pyrex glass tube (capacity, 20 mL) using a 2 kW Xe lamp (\( \lambda > 300 \) nm; Ushio Inc.) with magnetic stirring at 298 K. The light intensity was determined by a spectroradiometer to be 192.7 W m\textsuperscript{-2} at 300–800 nm. The light intensity at 300–400 nm, which mainly contributes to the photocatalytic reaction, is therefore calculated from the spectral irradiance to be 18.2 W m\textsuperscript{-2}. The reactant and product concentrations were determined by GC-FID or -TCD, using authentic samples as standards.

2-3. Analysis

The total Pd and Pt amounts of the catalysts were analyzed by an inductively-coupled argon plasma atomic emission spectrophotometer (Seiko Instruments, Inc.; SPS7800) after dissolution of the catalysts to an aqua regalia. Diffuse reflectance UV-vis spectra were measured on UV-vis spectrophotometer (Jasco Corp.; V-550 with Integrated Sphere Apparatus ISV-469) with BaSO\textsubscript{4} as a reference. TEM
observations were carried out using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV, which is equipped with an Energy Dispersive X-ray Spectroscopy (EDX) detector. EDX spectra from a metallic particle were taken under Scanning Transmission Electron Microscopy (STEM) mode. XPS measurements were performed using a JEOL JPS-9000MX spectrometer using Mg Kα radiation as the energy source.

3. Results and discussion

3-1. Synthesis and characterization of catalysts

Pd\textsubscript{1}Pt\textsubscript{5}/TiO\textsubscript{2} with Pd-Pt alloy consisting of 1 wt% Pd [\(= \frac{\text{Pd}}{\text{Pd} + \text{TiO}_2} \times 100\)] and different amounts of Pt [\(y \text{ (wt\%) = } \frac{\text{Pt}}{\text{Pt} + \text{TiO}_2} \times 100\)] were prepared with Japan Reference Catalyst JRC-TIO-4 TiO\textsubscript{2} (equivalent to Degussa P25) by simultaneous impregnation of Pd(NO\textsubscript{3})\textsubscript{2} and H\textsubscript{2}PtCl\textsubscript{6} followed by reduction with H\textsubscript{2}.\textsuperscript{5} A transmission electron microscopy (TEM) image of Pd\textsubscript{1}Pt\textsubscript{5}/TiO\textsubscript{2} showed spherical metal particles with an average diameter of 2.9 nm (Figure 4-1). The lower or higher Pt loadings create smaller or larger particles; Pd\textsubscript{1}Pt\textsubscript{1} and Pd\textsubscript{1}Pt\textsubscript{10} contain 2.5 and 3.4 nm particles, respectively. An X-ray photoelectron spectroscopy (XPS) of catalysts confirmed the presence of both Pd and Pt (Figure 4-2). An energy dispersive X-ray spectroscopy (EDX) of metal particles on Pd\textsubscript{1}Pt\textsubscript{5}/TiO\textsubscript{2} (Figure 4-3) determined the average Pt/Pd ratio as 4.95 (wt/wt), which is close to the ratio of the total amount of Pt and Pd (4.96) determined by ICP analysis. An X-ray diffraction (XRD) pattern of Pd\textsubscript{1}Pt\textsubscript{5}/TiO\textsubscript{2} (Figure 4-4) shows a (111) diffraction of the Pd-Pt alloy at 39.9°, which is located between the Pt(111) and Pd(111) diffractions (39.81 and 40.21). The lattice parameter of the alloy calculated from the XRD data (\(a = 0.391 \text{ nm}\)) agrees with that calculated with the Vegard's law\textsuperscript{6} (0.391 nm). In addition, the \(d\)-value calculated from the lattice spacing of the alloy in the TEM image (\(d_{111} = 0.225 \text{ nm, Figure 4-5}\)) is in between the standard Pt (\(d_{111} = 0.2265 \text{ nm, JCPDS 04-0802}\)) and Pd (\(d_{111} = 0.2246 \text{ nm, JCPDS 46-1043}\)). These indicate that Pd-Pt alloy particles are indeed loaded on TiO\textsubscript{2}. Diffuse reflectance UV-vis spectra (Figure 4-6) revealed that Pd\textsubscript{1}Pt\textsubscript{5}/TiO\textsubscript{2} with higher Pt loadings show increased absorbance at >300 nm due to light scattering by the Pt particles.
Figure 4-1. (a) TEM image of Pd$_3$/TiO$_2$ and (b) size distribution of metal particles on (white) the fresh catalyst and (black) the catalyst recovered after 2nd reuse in reaction (Table 1, run 16).

![TEM image of Pd$_3$/TiO$_2$ and size distribution of metal particles](image)

Figure 4-2. XPS results for respective catalysts.
Figure 4-3. TEM and STEM-HAADF images of Pd, Pt/TiO₂ and EDX spectra for respective metal particles.
Figure 4-4. XRD patterns of respective catalysts.

Figure 4-5. High-resolution TEM image of Pd$_x$Pt$_y$/TiO$_2$. 

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Figure 4-6. Diffuse reflectance UV-vis spectra of respective catalysts.
### 3-2. Photocatalytic activity of PdPt/TiO₂ catalysts

**Table 4-1.** Results of dechlorination of p-chlorotoluene in the photocatalytic and H₂ system.¹

![Chemical structure of p-chlorotoluene and products](image)

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Metal</th>
<th>Photocatalytic system</th>
<th>H₂ system</th>
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<tr>
<td></td>
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<td>particle</td>
<td></td>
</tr>
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<td></td>
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<td></td>
<td>size b / nm</td>
<td>conv. / %</td>
</tr>
<tr>
<td>1</td>
<td>Pd₅/TiO₂</td>
<td>5.3</td>
<td>20</td>
<td>19</td>
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<tr>
<td>2</td>
<td>Pd₇/TiO₂</td>
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<tr>
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<td>Pd₉/TiO₂</td>
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<td>41</td>
</tr>
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<td>Pd₁₁/TiO₂</td>
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<td>Pd₁₃/TiO₂</td>
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<td>Pd₁₅/TiO₂</td>
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<td>Pd₁₇/TiO₂</td>
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<td>76</td>
<td>76</td>
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<td>Pd₁₉/TiO₂</td>
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<td>38</td>
<td>80</td>
</tr>
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<td>9</td>
<td>Pd₁₁₁/TiO₂</td>
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<td>35</td>
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<td>Pt₁/TiO₂</td>
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<tr>
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<td>12</td>
<td>Pt₅/TiO₂</td>
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<td>Pt₇/TiO₂</td>
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<tr>
<td>14</td>
<td>Pd₁₁+Pt₇/TiO₂</td>
<td>27</td>
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<td>Pt₅/Pd₇/TiO₂</td>
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<td></td>
</tr>
<tr>
<td>16</td>
<td>Pt₅/Pd₇/TiO₂</td>
<td>3.1 f</td>
<td>75</td>
<td>75</td>
</tr>
</tbody>
</table>

¹ The results obtained with Pd₁₁₁/TiO₂ in other solvents are summarized in Table 4-2. b Average diameter of metal nanoparticles determined by TEM observation (Figure 5-1). c Determined by eqn (8). d 1st reused after washing with 2-PrOH. e 2nd reuse. f Measured after 2nd reuse.

Table 4-1 summarizes the results of photocatalytic reaction (λ >300 nm) of p-chlorotoluene (0.2 mmol) in 2-PrOH (5 mL) with catalysts (5 mg) and NaOH (0.5 mmol) for 1 h at 298 K under Ar. The results obtained using H₂ (1 atm) in the dark at 298 K are also shown for comparison. Both
photocatalytic and H₂ systems (runs 1–9) selectively produce toluene. The toluene yields in the photocatalytic system with the catalysts containing Pd alone, Pdₓ/TiO₂ [ₓ (wt%) = Pd/TiO₂ × 100], are less than 21% (runs 1–4). In contrast, the yields in the H₂ system with Pdₓ/TiO₂ are ca. 50%, indicating that the photocatalytic system is indeed inefficient.

The loading of Pd-Pt alloy particles significantly enhances the photocatalytic dechlorination (runs 5–9): PdₓPtᵧ/TiO₂ show increased toluene yields with an increase in the Pt amount of the particles, where PdₓPtᵧ/TiO₂ shows the highest yield (76%), which is more than three times that of Pdₓ/TiO₂. In contrast, such alloying effect is not observed in the H₂ system (runs 5–9); the toluene yields decrease monotonically with the Pt loadings (<56%).

It is noted that the catalysts containing Pt alone, Ptᵧ/TiO₂ [ᵧ (wt%) = Pt/TiO₂ × 100], do not promote dechlorination (runs 10–13). This indicates that, on the alloy catalysts, the Pd site is active for dehalogenation. It is also noted that the Pd-Pt alloy site is necessary for efficient dehalogenation: a PdₓPtᵧ/TiO₂ catalyst (run 14), prepared by a step-by-step deposition of respective Pd and Pt particles, scarcely enhances dehalogenation.

Table 4-2. Results of photocatalytic dechlorination of p-chlorotoluene in various solvent.¹

<table>
<thead>
<tr>
<th>Run</th>
<th>Solvent</th>
<th>p-chlorotoluene conv. / %</th>
<th>Toluene yield / %</th>
<th>Aldehyde or ketone formed / μmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Water/MeCN</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1/1 v/v)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>EtOH</td>
<td>8</td>
<td>7</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>2-PrOH</td>
<td>76</td>
<td>76</td>
<td>155</td>
</tr>
<tr>
<td>5</td>
<td>n-butanol</td>
<td>5</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>n-hexanol</td>
<td>2</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

¹ the reaction conditions are identical to those of Table 4-1.
3-3. Reaction mechanism

Scheme 4-1. The reaction sequence for protons on the metal particles of (a) Pd,Pt,TiO₂ and (b) Pd₁+Pt₅/TiO₂ catalysts.

The high activity of the alloy catalyst is due to the efficient consumption of photoformed e⁻ by H⁺ reduction on the Pt site and efficient transfer of the formed H atom to the adjacent Pd site (Scheme 4-1a). The efficient e⁻ consumption on Pt is confirmed by the amount of formed acetone (Table 4-1). Pd₁/TiO₂ produce <45 μmol acetone (runs 1–4), whereas Pt₅/TiO₂ produce larger amounts (runs 10–13). This is because e⁻ is efficiently trapped by Pt due to the larger work function and consumed by H⁺ reduction, facilitating efficient alcohol oxidation by h⁺. As shown in run 12, Pt₅/TiO₂ produces the largest amount of acetone among Pt₅/TiO₂ and higher Pt loadings decrease the production. A similar tendency is observed for Pd₃Pt₅/TiO₂: Pd₁Pt₅ produces the largest amount of acetone. The higher activity of Pd₃Pt₅/TiO₂ than Pd/TiO₂ is thus because the photoformed e⁻ is efficiently consumed by H⁺ reduction on the Pt site, producing a H atom.

H⁺ + e⁻ + Pt → H–Pt

The H atom on Pt within the alloy particles is efficiently used for dehalogenation. This is confirmed by the H⁺ balance, defined as the ratio of the formed dehalogenation product to that of the formed H⁺. As shown by eqn (6), two H⁺ formed by photooxidation of 2-PrOH are consumed by dehalogenation (eqn (3) and (4)) and reaction with NaOH (eqn (5)), respectively. The H⁺ balance is therefore expressed by the ratio of the amount of formed toluene to that of formed acetone,

H⁺ balance = [toluene formed]/[acetone formed]

Table 4-1 summarizes the H⁺ balance for the respective systems obtained by photoreaction for 1 h. The values for Pd₁/TiO₂ are almost 1 (runs 1–4), indicating that H⁺ formed by alcohol oxidation are
consumed quantitatively by dehalogenation on Pd (eqn (6)). The values for PdPt/TiO₂ are also almost 1 (runs 5–9), suggesting that H⁺ are also consumed quantitatively although H⁺ are reduced on Pt (eqn (7)). The results suggest that, as shown in Scheme 4-1a, the H atom formed on Pt is transferred to the adjacent Pd site (H–Pd formation), which is probably due to the stronger H–Pd interaction.

\[ \text{H–Pt} \rightarrow \text{H–Pd} \]  
\[ \text{(9)} \]

The H atom is reduced to the hydride species (H⁻–Pd) by e⁻, which promotes dechlorination (eqn (4))

\[ \text{H–Pd} + \text{e}^- \rightarrow \text{H}^-\text{Pd} \]  
\[ \text{(10)} \]

As shown in run 14, the H⁻ balance for the Pd₁₊₆/Pt₅/TiO₂ system is only 0.44. This is because the absence of Pd around the Pt site suppresses the H transfer from Pt to Pd and results in removal of H atoms by H₂ formation (Scheme 4-1b).

\[ \text{H}^-\text{Pt} + \text{H}^-\text{Pt} \rightarrow \text{H}_2 \uparrow + 2\text{Pt} \]  
\[ \text{(11)} \]

Change in H₂ amount during reaction confirms this (Figure 4-7). Pd₁₊₆/Pt₅/TiO₂ promotes H₂ formation and dechlorination simultaneously; however, Pd₅/Pt₅/TiO₂ scarcely produces H₂ until p-chlorotoluene disappears. The alloy sites are therefore necessary for efficient H transfer from the Pt to Pd sites.

The above results reveal that, on the alloy site (Scheme 4-1a), efficient reduction of H⁻ by e⁻ on Pt, smooth H transfer to Pd, and reduction of H by e⁻ occur sequentially. This sequence produces a large amount of H⁻–Pd species and promotes efficient dehalogenation. It must be noted that, as shown in runs 15 and 16 (Table 4-1), the alloy catalyst is reusable for dehalogenation at least two times without loss of activity and selectivity. In addition, as shown in Figure 4-1b, the size of Pd-Pt alloy particles scarcely changes even after the reaction.
Figure 4-7. Time-dependent change in the amounts of substrate and products during photoinadiation of a 2-PrOH solution containing p-chlorotoluene with Pd$_1$+Pt$_5$/TiO$_2$ or Pd$_1$Pt$_5$/TiO$_2$ catalyst. The reaction conditions are identical to those in Table 4-1.
3-4. Dehalogenation of various aromatic halides

Table 4-3. Dehalogenation of various aromatic halides.

The alloy catalyst is tolerant for photocatalytic dehalogenation of various aromatic halides (Table 4-3). Pd\textsubscript{1}Pt\textsubscript{2}/TiO\textsubscript{2} produces the corresponding dehalogenation compounds with very high yield, and the catalytic activities are much higher than those obtained with Pd\textsubscript{1}/TiO\textsubscript{2} using H\textsubscript{2}.

4. Conclusion

In summary, we found that UV irradiation of TiO\textsubscript{2} loaded with Pd-Pt alloy promotes efficient dehalogenation. This offers crucial advantages: (i) safe alcohols can be used as a hydrogen source; and, (ii) the reaction proceeds much faster. The alloy catalyst that facilitates efficient production of active species (H\textsuperscript{—}–Pd) may also promote other hydrogenation reactions, and the work along these lines is currently in progress.
5. References


Chapter V

Partial Oxidation of Cyclohexane on WO₃ Loaded with Pt Nanoparticles under Visible Light Irradiation

1. Introduction

The partial oxidation of cyclohexane (CHA) to cyclohexanol (CHA-ol) and cyclohexanone (CHA-one) has attracted much attention because these products are the intermediates in e-caprolactam synthesis.¹ Of particular interest is the catalytic CHA oxidation in heterogeneous systems with molecular oxygen (O₂).² Photocatalytic CHA oxidation with O₂ has also been studied extensively with various catalysts such as TiO₂,³ Fe porphyrin-modified TiO₂,⁴ polyoxotungstate-modified SiO₂,⁵ and V₂O₅-impregnated Al₂O₃.⁶ Some of these systems promote partial oxidation of CHA with high selectivity (>89%).³⁶ All of these systems, however, require UV light for catalyst activation. Earlier, we reported that Cr-containing silica with highly dispersed chromate species catalyzes partial oxidation of CHA under visible light with high selectivity (>99%).⁷ Cr species are, however, very toxic to living organisms;⁸ therefore, an alternative Cr-free photo-catalytic system is desirable for clean production of CHA-ol and CHA-one.

Photocatalytic oxidation of CHA on TiO₂ proceeds via the following mechanism.³⁶ Photoexcitation of TiO₂ produces the electron (e⁻) and positive hole (h⁺) pairs. The h⁺ oxidizes CHA (C₆H₁₂) and produces a cyclohexyl radical (C₆H₁₁•). This radical reacts with O₂ and produces a peroxy radical (C₆H₁₁OO•).

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow h^+ + e^- \\
\text{C}_6\text{H}_{12} + h^+ & \rightarrow \text{C}_6\text{H}_{11}^\cdot + \text{H}^+ \\
\text{C}_6\text{H}_{11}^\cdot + \text{O}_2 & \rightarrow \text{C}_6\text{H}_{11}\text{OO}^\cdot
\end{align*}
\]

Combination of the peroxy radicals produces CHA-ol (C₆H₁₁OH) and CHA-one (C₆H₁₀O).

\[
\text{C}_6\text{H}_{11}\text{OO}^\cdot + \text{C}_6\text{H}_{11}\text{OO}^\cdot \rightarrow \text{C}_6\text{H}_{11}\text{OH} + \text{C}_6\text{H}_{10}\text{O} + \text{O}_2
\]

The e⁻ on TiO₂ is consumed by a single-electron reduction of O₂, producing a superoxide anion (O₂•⁻). This reacts with C₆H₁₁• and produces CHA-one.

\[
\begin{align*}
\text{O}_2 + e^- & \rightarrow \text{O}_2^\cdot ( -0.13 \text{ V vs. NHE}) \\
\text{C}_6\text{H}_{11}^\cdot + \text{O}_2^\cdot & \rightarrow \text{C}_6\text{H}_{10}\text{O} + \text{OH}^-
\end{align*}
\]
Selective production of CHA-ol and CHA-one on TiO₂ is, however, difficult. One of the reasons is that CHA is decomposed simultaneously during the reactions: the formed peroxy radical (C₆H₁₁OO⁺) reacts with h⁺ and is decomposed to CO₂ via the C–C bond cleavage.⁹

\[ \text{C}_6\text{H}_{11}\text{OO}^+ + \text{h}^+ \rightarrow \text{decomposition (CO}_2\text{ formation)} \]  

(7)

Another reason is that the formed CHA-ol and CHA-one are decomposed subsequently by photocatalytic reactions, producing CO₂.⁸ Although the detailed mechanism for decomposition has not been clarified, it is considered that the oxidation of these compounds by h⁺ (radical formation) and the reaction with O₂⁻ are involved in the mechanism.

\[ \text{C}_6\text{H}_{11}\text{OH (or C}_6\text{H}_{10}\text{O)} + \text{h}^+ + \text{O}_2^- \rightarrow \text{decomposition (CO}_2\text{ formation)} \]  

(8)

This suggests that O₂⁻, produced via the reduction of O₂ by the conduction band e⁻ on TiO₂ (eqn (5)), promotes decomposition of CHA-ol and CHA-one. Therefore, if the formation of O₂⁻ is suppressed, the decomposition of these partial oxidation products would be inhibited.

WO₃ is a semiconductor material that is excited by visible light irradiation (λ < 443 nm). There are, however, only a few reports of photocatalytic reactions on WO₃ because of its low activity. As shown in Scheme 5-1, the conduction band potential of WO₃ (+0.5 V vs.NHE) is more positive than the potential for single-electron reduction of O₂ (eqn (5), −0.13 V). The photoformed e⁻ on WO₃ is therefore not consumed efficiently by O₂, resulting in low catalytic activity. A recent report, however, revealed that the WO₃ loaded with Pt particles (Pt/WO₃) exhibits enhanced catalytic activity for degradation of acetic acid and acetaldehyde under visible light. This is because the conduction band e⁻ of WO₃ is consumed efficiently on the Pt particles by the promotion of a multi-electron reduction of O₂ as follows.

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 (+0.68 \text{ V vs. NHE)} \]  

(9)

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O (+1.23 \text{ V vs. NHE)} \]  

(10)

On the Pt/WO₃ system, the formation of O₂⁻ that promotes subsequent decomposition of CHA-ol and CHA-one (eqn (8)) is unfavorable. This system, if employed for CHA oxidation, would promote partial oxidation under visible light.
In the present work, the Pt/WO₃ catalysts were employed for photocatalytic oxidation of CHA with O₂ under visible light. The catalysts successfully promote partial oxidation with ca. 93% selectivity. The ESR measurements with a spin trapping reagent and the photocatalytic reactions with an O₂•⁻ scavenger indicate that selective oxidation of CHA on Pt/WO₃ is indeed achieved due to the decreased formation of O₂•⁻.

2. Experimental

2-1. Materials

WO₃ particles were supplied from Kojundo Chem. Lab. Co. (diameter, 128.0 nm; BET surface area, 3.1 m² g⁻¹). JRC-TIO-4 TiO₂ particles (equivalent to Degussa P25, diameter, 25.8 nm, BET surface area; 54.0 m² g⁻¹) were kindly supplied from the Catalysis Society of Japan. Other reagents were purchased from Wako, Tokyo Kasei, and Sigma-Aldrich and used without further purification. Water was purified by the Milli Q system.

2-2. Catalyst preparation

Ptₓ/WO₃ catalysts with different Pt loadings [x (wt%) = Pt/(Pt + WO₃) × 100; x = 0.1, 0.2, 0.3, 0.6, 1.3] were prepared as follows: WO₃ particles (0.1 g) and H₂PtCl₆ (0.34, 0.42, 0.61, 1.31, 2.77 mg) were added to a water/MeOH (24/1 v/v) mixture (10 mL) in a Pyrex glass tube (20 cm³; φ 10 mm). The tubes were purged with N₂ gas and photoirradiated using a high-pressure Hg lamp (300 W; Eikohsha Co. Ltd.; light intensity at 300–500 nm, 32.9 W m⁻²) with magnetic stirring at 303 K for 30 min. The catalysts
were recovered by filtration, washed with water, and dried in vacuo at 353 K for 12 h.

2-3. Photoreaction

The catalysts (10 mg) were added to a CHA/MeCN (1/9 v/v, 10 mL) mixture in a Pyrex glass tube (20 cm³; φ 10 mm). The tubes were purged with O₂ gas and photoirradiated with magnetic stirring by a Xe lamp (2 kW; Ushio Inc.), filtered through an aqueous NaNO₂ (20 wt%) solution to give light wavelengths of λ >420 nm. The temperature of solution during irradiation was 303 K. After the reaction, the gas phase product was analyzed by GC-TCD (Shimadzu; GC-14B). The resulting solution was recovered by centrifugation and analyzed by GC-FID (Shimadzu; GC-1700).

2-4. ESR measurement

ESR spectra were recorded at the X-band using a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 1.0 mW, where the microwave power saturation of the signals does not occur. The magnetic field was calibrated using 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as a standard. CHA/MeCN (1/9 v/v, 10 mL) mixture, catalyst (10 mg), and 5,5'-dimethyl-1-pyrroline-N-oxide (DMPO, 25 mM) were added to a Pyrex glass tube (20 cm³). The tube was purged with O₂ and photoirradiated using a Xe lamp for 3 min under magnetic stirring at 303 K. The solution was recovered by filtration, and ESR measurement was carried out at 298 K.

2-5. Analysis

The Pt amount on the catalysts was determined by an X-ray fluorescence spectrometer (Seiko Instruments Inc.; SEA2110). Diffuse reflectance UV-vis absorption spectra were measured on a JASCO V-550 spectrophotometer. The light intensity was measured with a spectroradiometer (USR-40, Ushio Inc.). The H₂O₂ amount in solution was determined by an iodometric titration; the reaction mixture recovered by filtration was treated with an excess amount of NaI and the amount of I₃⁻ formed was determined with UV-vis analysis at 361 nm (ε = 2.0 × 10³ M⁻¹ cm⁻¹ in CHA/MeCN (1/9 v/v) mixture) using an UV-visible spectrophotometer (Shimadzu; Multispec-1500).

3. Results and discussion
3-1. Catalyst properties

The Ptₓ/WO₃ catalysts with different Pt loadings [x (wt%) = Pt/(Pt + WO₃) × 100] were prepared by
a photodeposition method (Table 5-1). UV irradiation of a water/MeOH mixture containing WO₃ particles and different amounts of H₂PtCl₆ produces dark yellow powders of catalysts. As shown in Figure 5-1a, the high resolution transmission electron microscopy (HRTEM) image of the Pt₈₀/WO₃ catalyst reveals that isolated hemispherical Pt nanoparticles are supported on WO₃. The mean diameter of the Pt particles was determined to be 4.7 nm. The size of Pt particles is scarcely affected by the Pt loadings; Pt₄/WO₃ contains 4.8 nm Pt particles (Figure 5-1b). Figure 5-2 shows the diffuse reflectance UV-vis absorption spectra of catalysts. The Pt/WO₃ catalysts with larger Pt loadings show increased absorbance at λ >400 nm due to the light scattering by the Pt particles, although the band gap energies of catalysts are similar (2.6–2.8 eV).

Figure 5-1. Typical cross-sectional HRTEM image and size distribution of Pt particles on (a) Pt₈₀/WO₃ and (b) Pt₄/WO₃. The black bars are the data for fresh catalysts and the white bars are the data for catalysts after the reuse reactions (Table 5-1, run 11).
3-2. Photocatalytic activity

Table 5-1. Results of photooxidation of cyclohexane (CHA) with various catalysts.\(^a\)

<table>
<thead>
<tr>
<th>run</th>
<th>catalyst</th>
<th>Pt particle size(^b) / nm</th>
<th>CHA-ol yields / µmol</th>
<th>CHA-one yields / µmol</th>
<th>CO(_2) yields / µmol</th>
<th>selectivity for partial oxidation / %</th>
<th>H(_2)O(_2) formed / µmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WO(_3)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>92</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pt(_{0.1})/WO(_3)</td>
<td>4.3</td>
<td>3.8</td>
<td>3.9</td>
<td>93</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pt(_{0.2})/WO(_3)</td>
<td>4.7</td>
<td>4.4</td>
<td>4.2</td>
<td>93</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Pt(_{0.3})/WO(_3)</td>
<td>3.7</td>
<td>3.3</td>
<td>2.9</td>
<td>94</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
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<td>Pt(_{0.6})/WO(_3)</td>
<td>3.4</td>
<td>3.1</td>
<td>2.9</td>
<td>93</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pt(_{1.3})/WO(_3)</td>
<td>4.8</td>
<td>3.2</td>
<td>2.7</td>
<td>93</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>TiO(_2)</td>
<td>1.4</td>
<td>2.6</td>
<td>11.6</td>
<td>67</td>
<td>0.5</td>
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</tr>
<tr>
<td>8</td>
<td>Pt(_{0.2})/TiO(_2)</td>
<td>2.0</td>
<td>1.8</td>
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<td>12.9</td>
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</tr>
<tr>
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<td>1st reuse</td>
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<td>4.6</td>
<td>4.3</td>
<td>93</td>
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<td></td>
</tr>
<tr>
<td>10</td>
<td>2nd reuse</td>
<td>4.0</td>
<td>4.4</td>
<td>4.0</td>
<td>93</td>
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<td></td>
</tr>
<tr>
<td>11</td>
<td>3rd reuse</td>
<td>4.8</td>
<td>3.8</td>
<td>3.9</td>
<td>93</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: CHA/MeCN (1/9 v/v, 10 mL), catalyst (10 mg), \(\lambda > 420\) nm, O\(_2\) (1 atm), photoirradiation time, 12 h. \(^b\) determined by TEM analysis. \(^c\) = \([(\text{CHA-ol} + \text{CHA-one})/(\text{CHA-ol} + \text{CHA-one} + (1/6)\text{CO}_2)] \times 100\) (refs. 3d and 6b). \(^d\) prepared by a photodeposition method similar to Pt/WO\(_3\). \(^e\) Pt\(_{0.3}\)/WO\(_3\) reused after simple washing with MeCN. \(^f\) Determined after the reaction.
Table 5-1 summarizes the results of photocatalytic oxidation of CHA. The reactions were performed by visible light irradiation (λ >420 nm) of a CHA/MeCN (1/9 v/v) mixture with catalyst and O₂ for 12 h. As shown in run 1, pure WO₃ is inactive for oxidation, where only a small amount of CHA-ol and CHA-one is produced (both 0.7 μmol). The Pt loadings onto WO₃ enhance oxidation. As shown in runs 2–6, the Pt/WO₃ catalysts produce larger amounts of CHA-ol and CHA-one (>2.7 μmol). The selectivity for these products is ca.93%. Run 7 shows the results obtained with a common TiO₂ catalyst (anatase/rutile = 8/2); the CHA-ol and CHA-one yields are much lower than those obtained with Pt/WO₃, although the amount of CO₂ formed is much higher. The partial oxidation selectivity is 67%, which is lower than that obtained with Pt/WO₃. In addition, as shown in run 8, the Pt loading onto TiO₂ does not enhance the selectivity and yields. These findings indicate that the Pt/WO₃ system promotes selective and efficient photooxidation of CHA.

![Graph](image-url)

**Figure 5-3.** Time-dependent change in the yields of CHA-ol, CHA-one, and CO₂ formed during photooxidation of CHA (1 mL, 9.3 mmol) in MeCN with (a) Pt₀.₂/WO₃ and (b) TiO₂. Reaction conditions are identical to those in Table 5-1.

**Figure 5-3** shows the time-dependent change in the amounts of CHA-ol, CHA-one, and CO₂ produced during the photocatalytic oxidation of CHA with Pt₀.₂/WO₃ or TiO₂ catalyst. With TiO₂ (Figure 5-3b), the amount of CO₂ formed is much larger than those of CHA-ol and CHA-one. In contrast, with Pt₀.₂/WO₃ (Figure 5-3a), the CO₂ amount is comparable to those of CHA-ol and CHA-one. This again suggests that Pt/WO₃ indeed produces CHA-ol and CHA-one selectively, while suppressing...
Among the Pt/WO₃ catalysts (runs 2–6), Pt₀.₂/WO₃ (run 3) shows the highest yields of CHA-ol (4.3 pmol) and CHA-one (4.4 pmol). The catalysts with larger Pt loadings show decreased yields. This is probably because excess amount of Pt increases the absorbance at λ >400 nm, as shown in Figure 5-2, and suppresses the incident light absorption by WO₃. It is noted that the catalyst is reusable for reactions. As shown in runs 9–11, the Pt₀.₂/WO₃ catalyst, when reused for further reactions, shows the selectivity and yields similar to those of the virgin catalyst (run 3). In addition, HRTEM analysis of the catalyst recovered after the reuse revealed that the Pt particle size scarcely changes during reactions (Figure 5-1a). These indicate that the catalyst is reusable without loss of activity and selectivity.

3-3. Multi-electron reduction on WO₃

![Graph showing the formation of H₂O₂ over time](image)

**Figure 5-4.** Time-dependent change in the amount of H₂O₂ formed during photooxidation of CHA (1 mL, 9.3 mmol) in MeCN with TiO₂, WO₃, or Pt₀.₂/WO₃ catalyst. Reaction conditions are identical to those in Table 5-1.

On the photoexcited TiO₂, the conduction band e⁻ is mainly consumed by single-electron reduction of O₂ (O₂⁻ formation, eqn (5)). In contrast, on Pt/WO₃, this reduction is difficult because the conduction band potential of WO₃ is more negative than the potential of single-electron reduction of O₂ (Scheme 5-1). The enhanced oxidation of CHA by the Pt loadings on WO₃ (Table 5-1) is due to the efficient consumption of e⁻ on WO₃ by a multi-electron reduction of O₂, producing H₂O₂ or H₂O (eqn (9) and (10)). This is confirmed by the amount of H₂O₂ formed during photooxidation of CHA. As shown in Figure 5-4, the amount of H₂O₂ formed after 12 h photoirradiation with Pt₀.₂/WO₃ is 3.3 µmol,

CO₂ formation.
whereas pure WO₃ and TiO₂ produce smaller amounts. As summarized in Table 5-1 (final column), the H₂O₂ amount increases with the Pt loadings on WO₃, but the catalysts with >0.2 wt% Pt produce decreased amount of H₂O₂. This tendency is consistent with the oxidation activity of CHA (Table 5-1). These data clearly indicate that the multi-electron reduction of O₂ promoted on the Pt particles efficiently consumes the conduction band e⁻ of WO₃ and enhances CHA oxidation.

![ESR spectra](image)

**Figure 5-5.** ESR spectra for DMPO–O₂⁻ spin adduct signals obtained by photoirradiation of O₂-saturated CHA/MeCN (1/9 v/v) mixture containing DMPO with WO₃, Pt₀.₂/WO₃, or TiO₂ in the absence and presence of p-BQ (0.05 mmol). Reaction conditions: catalyst (10 mg), DMPO (0.25 mmol), CHA/MeCN (1/9 v/v, 10 mL), O₂ (1 atm), irradiation time (3 min).

On the Pt/WO₃ catalyst, the single-electron reduction of O₂ is indeed difficult. This is confirmed by ESR analysis. Figure 5-5 shows the spectra obtained after photoirradiation of an O₂-saturated CHA/MeCN (1/9 v/v) mixture with catalysts in the presence of DMPO, a spin-trapping reagent. All of the catalysts show distinctive signals assigned to the DMPO–O₂⁻ spin adduct (α_N = 13.0 G; α_H = 10.3 G, g = 2.0062). The spin adduct signal is observed on WO₃, although its conduction band potential is more positive than the potential of single-electron reduction of O₂ (Scheme 5-1). As also observed for the related WO₃ system, this is probably attributable to the negative shift of particle charge due to the effect of electrical potential floating in non-aqueous media or the energy level spreading due to the distribution of reduction potential of O₂. The intensity of the spin adduct signal observed on Pt₀.₂/WO₃ is
much weaker than that on TiO$_2$. This clearly indicates that the single-electron reduction of O$_2$ is indeed unfavorable on Pt/WO$_3$ and a lower amount of O$_2^-$ is produced.

3-4. Suppression of subsequent decomposition of products

The selective formation of partial oxidation products on Pt/WO$_3$ is because the catalyst suppresses subsequent photocatalytic decomposition of the CHA-ol and CHA-one produced. In contrast, TiO$_2$ decomposes these products and produces CO$_2$, as denoted by eqn (8). Figure 5-6 shows the time-dependent change in the amount of CO$_2$ formed during photoreaction of 0.1 mmol of CHA, CHA-ol, or CHA-one as the starting material. With TiO$_2$ (white circle), CO$_2$ is scarcely formed from CHA (Figure 5-6a), but is produced significantly from CHA-ol and CHA-one (Figure 5-6b and c). This indicates that, in the CHA photooxidation on TiO$_2$ (Figure 5-3b), the formed CHA-ol and CHA-one are subsequently decomposed, resulting in small amounts of CHA-ol and CHA-one and a large amount of CO$_2$. In contrast, on Pt$_{0.2}$/WO$_3$ (Figure 5-6b and c; black circle), the CO$_2$ production from CHA-ol and CHA-one is much suppressed. This indicates that, in the CHA photooxidation on Pt$_{0.2}$/WO$_3$ (Figure 5-3a), further decomposition of the products is suppressed, resulting in large amounts of CHA-ol and CHA-one and a relatively small amount of CO$_2$.

![Figure 5-6](image_url)

Figure 5-6. The amount of CO$_2$ formed during photooxidation of 0.1 mmol of (a) CHA, (b) CHA-ol, and (c) CHA-one with TiO$_2$ or Pt$_{0.2}$/WO$_3$ in the absence/presence of p-BQ (0.05 mmol) or KI (0.05 mmol). Reaction conditions: catalyst (10 mg), substrate (0.1 mmol), MeCN (10 mL), λ >420 nm, O$_2$ (1 atm). The light intensity at 420–500 nm is 26.9 W m$^{-2}$. 

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The decreased decomposition of CHA-ol and CHA-one on Pt/WO₃ is due to the suppression of O₂•⁻ formation. To clarify this, the effect of p-benzoquinone (p-BQ), an O₂•⁻ quencher, on the photocatalytic decomposition of CHA-ol and CHA-one with TiO₂ was studied. As shown in Figure 5-5, the ESR signal for the DMPO–O₂•⁻ adduct obtained with TiO₂ in the presence of p-BQ is much weaker than that obtained with TiO₂ alone, indicating that p-BQ indeed quenches O₂•⁻. Figure 5-6(b) and (c) show the amount of CO₂ formed during photoreaction of CHA-ol and CHA-one with TiO₂ in the presence of p-BQ. The addition of p-BQ decreases the CO₂ formation. This indicates that the decomposition of partial oxidation products is indeed promoted by O₂•⁻.

Figure 5-7. The yields of products formed by photooxidation of CHA (1 mL, 9.3 mmol) for 12 h with (a) Pt₀.₂/WO₃ and (b) TiO₂ catalysts at different light intensities (420–500 nm). Reaction conditions are identical to those in Table 5-1.

The involvement of O₂•⁻ in the decomposition of partial oxidation products is confirmed by photooxidation of CHA at different light intensities. Figure 5-7 shows the product yields after 12 h photoirradiation. With Pt₀.₂/WO₃ (Figure 5-7a), the yields of all products increase with the intensity increase, and the product selectivity is unchanged. This indicates that, under the suppressed O₂•⁻ formation condition, the decomposition of CHA-ol and CHA-one is not accelerated even by an increase in the amount of h⁺ formed on the catalyst; in other words, CO₂ formation is not promoted by the decomposition of CHA-ol and CHA-one but by the decomposition of a peroxy radical (C₆H₁₁OO•⁻) with
In contrast, with TiO$_2$ (Figure 5-7b), the intensity increase enhances CO$_2$ formation while decreasing the formation of CHA-ol and CHA-one. The increase in light intensity enhances O$_2$* formation (eqn (5)). This accelerates the decomposition of CHA-ol and CHA-one by O$_2$*- as proposed in eqn (8). These data clearly indicate that O$_2$*- is involved in the decomposition of partial oxidation products.

Effect of h$^+$ on the decomposition of partial oxidation products was studied. Potassium iodide (KI), a h$^+$ scavenger, was added to a MeCN solution containing CHA-ol or CHA-one together with TiO$_2$ and used for the photocatalytic reaction. As shown in Figure 5-6b and c, the addition of KI decreases CO$_2$ formation as compared to that obtained with TiO$_2$ alone. This suggests that the photoformed h$^+$ is also involved in the mechanism for decomposition of CHA-ol and CHA-one. These findings indicate that, as proposed in eqn (8), the decomposition of partial oxidation products is promoted by the combination of O$_2$*- and h$^+$. The decreased O$_2$* formation on the Pt/WO$_3$ catalyst, therefore, suppresses the decomposition and promotes selective formation of CHA-ol and CHA-one. As denoted by eqn (7), CHA is inevitably decomposed via the reaction of a peroxy radical with h$^+$. Further improvement is therefore necessary for more selective CHA oxidation. Nevertheless, the results presented here suggest that the suppression of O$_2$* formation is one of the efficient ways for selective production of CHA-ol and CHA-one by photocatalysis.

4. Conclusion

WO$_3$ loaded with Pt particles (Pt/WO$_3$) were used as catalysts for oxidation of CHA with O$_2$ under visible light. These catalysts successfully promote partial oxidation (formation of CHA-ol and CHA-one) with ca. 93% selectivity. The high selectivity for CHA oxidation on Pt/WO$_3$ is due to the decreased O$_2$* formation. This suppresses the photocatalytic decomposition of partial oxidation products occurring via the combination of h$^+$ and O$_2$*.

5. References


Chapter VI

Aerobic Oxidation by Platinum Nanoparticle Supported on Anatase Titanium Dioxide under Visible Light Irradiation

1. Introduction

Aerobic oxidation by heterogeneous catalysts with molecular oxygen (O₂) as an oxidant is an essential process for the synthesis of various chemicals.¹ Photocatalytic oxidation with O₂ has also been studied extensively with semiconductor materials such as titanium dioxide (TiO₂);²–⁶ several types of substrates such as alcohols, amines, hydrocarbons, and sulfides are successfully oxidized at atmospheric pressure and room temperature. One of the critical issues for practical application of photocatalytic processes is the low catalytic activity under irradiation of visible light (λ > 400 nm), the main component of solar irradiance. Several TiO₂ materials doped with nitrogen,⁷,⁸ sulfur,⁹,¹⁰ carbon,¹¹,¹² or boron atoms¹³ have been proposed to extend the absorption edge of catalysts into the visible region. These doped catalysts, however, suffer from low quantum yields for reaction (<0.5%), because they inherently contain a large number of crystalline lattice that acts as a charge recombination center.¹⁴ Development of visible-light-driven catalysts that promote highly efficient aerobic oxidation is still a challenge.

Nanosized noble metals such as gold (Au) and silver (Ag) absorb light in the visible region due to a resonant oscillation of free electrons coupled by light, known as localized surface plasmon resonance (SPR).¹⁵ Application potentiality of SPR to photocatalysis was first discovered by Tian et al.¹⁶ Visible light irradiation of Au particles loaded on a TiO₂ film that is coated on an indium tin oxide electrode generates an anodic photocurrent in the presence of Fe²⁺. This occurs via a collective oscillation of electrons (e⁻) on the Au particles induced by visible light and a subsequent transfer of e⁻ to the TiO₂ conduction band. Simultaneously, the positively charged Au particles receive e⁻ from the electron donor (Fe²⁺). This suggests that visible light irradiation successfully creates the charge-transfered state at the metal/semiconductor heterojunction and would promote catalytic oxidation and reduction reactions, i.e. plasmonic photocatalysis.¹⁷,¹⁸

Very recently, we found that visible-light-induced plasmonic photocatalysis successfully promotes aerobic oxidation of alcohols at the Au/semiconductor interface.¹⁹ This is achieved by Au particles loaded on a mixture of anatase/rutile TiO₂ (Degussa, P25). The activity of Au/P25 catalyst critically depends on its architecture; Au particles with ca. 4 nm diameter located at the interface of anatase/rutile TiO₂ are necessary. The plasmonic reaction on Au/P25 proceeds via the multistep e⁻ transfer, as summarized in Scheme 1. The photoactivated Au particles transfer e⁻ to rutile (a). The e⁻ is then
transferred to the adjacent anatase (b). O₂ is reduced on the anatase surface by e⁻ and produces a peroxo-type oxygen anion (O–O⁻) (c). Alcohol is adsorbed onto the positively charged Au particles via the interaction of its H atom with the O–O⁻ species, producing an Au–alcoholate species (d). Subsequent removal of H atom from the species produces the corresponding aldehydes or ketones (e). The apparent quantum yield for this reaction is 3.8% by the irradiation of 550 nm monochromatic light, which is much higher than that obtained with the doped photocatalysts (<0.5%). The metal/semiconductor system is chemically stable under aerated condition as compared to the doped photocatalysts. The plasmonic photocatalysis therefore has a potential for visible-light-induced aerobic oxidation.

Scheme 6-1. Aerobic oxidation of alcohol on the Au/P25 catalyst activated by visible light.

The next challenge is further activity improvement of the plasmonic photocatalysts. In the plasmonic reaction, the charge separation is facilitated by the reduction of O₂ on the semiconductor surface with the e⁻ transferred from the photoactivated metal particles. The anatase surface is active for O₂ reduction, whereas rutile surface is inactive. In contrast, photoactivated Au particles scarcely transfer e⁻ to anatase, probably due to the weak Au/anatase interaction, but the e⁻ transfer to rutile does occur. Therefore, as shown in Scheme 6-1, the Au/P25 system requires the Au→rutile→anatase multistep e⁻ transfers for reaction. This circuitous process may suppress smooth e⁻ transfer and decrease the reaction efficiency. In particular, the rutile→anatase e⁻ transfer (Scheme 6-1b) is probably the
rate-determining step. This is because the conduction band potential ($E_{CB}$) of rutile is more positive than $E_{CB}$ of anatase, and the rutile→anatase e⁻ transfer requires a negative shift of rutile $E_{CB}$ by the accumulation of e⁻ on its conduction band.²²,²³ Development of more efficient plasmonic photocatalysts therefore requires the creation of metal/anatase heterojunction that enables direct e⁻ transfer to anatase.

Pt particles also exhibit absorption band in the visible region, which is assigned to the intraband transition of electrons from sp band to the sp-conduction band (SPR absorption) and the interband transition of electrons from d band to sp-conduction band.²⁴ The intensity of this absorption is much weaker than that of Au particles.¹⁵ There is only one report of photocatalysis driven by visible light activation of Pt particles; Zhai et al.²⁵ reported that Pt particles loaded on a TiO₂ thin film promote dehydrogenation of alcohols by visible light ($\lambda > 420$ nm) under N₂ atmosphere. Herein, we report that Pt particles with 3–4 nm diameter loaded on anatase TiO₂, when used for aerobic oxidation under visible light, facilitate direct e⁻ transfer to anatase and promote the reaction highly efficiently. The Pt/anatase catalysts promote aerobic oxidation of alcohols with an apparent quantum yield 7.1% (550 nm), which is much higher than that obtained with the Au/P₂₅ catalyst (3.8%).¹⁹ In addition, the catalyst successfully promotes the reaction even under irradiation of sunlight.³

2. Experimental

2-1. Preparation of catalysts

Ptₓ₀⁹/TiO₂ catalysts [x (wt %) = 0.5, 1, 2, 3, 4; y (K) = 473, 573, 673, 773, 823, 873] were prepared as follows. TiO₂ (1.0 g) was added to water (20 mL) containing H₂PtCl₆·6H₂O (13.3, 26.8, 54.2, 82.1, or 110.6 mg). The solvents were removed by evaporation at 353 K with vigorous stirring. The obtained powders were calcined under air flow and then reduced under H₂ flow at the identical temperature (y). The heating rate was 2 K min⁻¹ and the holding time at the designated temperature was 2 h, respectively. Ptₓ₂₆₇₃/SiO₂ was prepared in a similar manner.

Auₓ/P₂₅ was prepared by the deposition-precipitation method as described previously.¹⁹ P₂₅ TiO₂ (1.0 g) was added to water (50 mL) containing HAuCl₄·4H₂O (45.8 mg). The pH of solution was adjusted to ca. 7 with 1 mM NaOH, and the solution was stirred at 353 K for 3 h. The particles were recovered by centrifugation, washed with water, and dried at 353 K for 12 h. The powders were calcined under air flow, where the heating rate was 2 K min⁻¹ and the holding time at 673 K was 2 h.

2-2. Reaction procedure

Catalyst (5 mg) was added to toluene (5 mL) containing an alcohol within a Pyrex glass tube (φ 10
mm; capacity, 20 mL), and the tube was sealed with a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min, and O₂ was bubbled through the solution for 5 min. The tube was immersed in a temperature-controlled water bath (298 ± 0.5 K) and photoirradiated at λ >450 nm with magnetic stirring using a 2 kW Xe lamp (USHIO Inc.), filtered through a CS3-72 glass (Kopp Glass Inc.). The light intensity at 450–800 nm was 16.8 mW cm⁻². Sunlight reactions were performed on 30th January, 2012 at 10:00–14:00 at the top of the laboratory building (north latitude 34.7°, east longitude 135.5°). The light intensity at 300–800 nm was 8.1 mW cm⁻² (Figure S6). The highest temperature of solution during the sunlight exposure was 293 K, and the dark experiments were carried out at 293 K. After the reactions, the catalyst was recovered by centrifugation, and the solution was subjected to GC-FID analysis, where the concentrations of substrates and products were calibrated with authentic samples.

2-3. Action spectra analysis

The photoreactions were carried out in a toluene solution (2 mL) containing 1 (0.4 mmol) with Pt₂(anatase or Au₂/P25 catalyst (8 mg) using a Pyrex glass tube. After ultrasonication and O₂ bubbling, the tube was photoirradiated using a 2 kW Xe lamp, where the incident light was monochromated by band pass glass filters (Asahi Techno Glass Co.). The full-width at half-maximum (FWHM) of the light was 11–16 nm. The photon number entered into the reaction vessel was determined with a spectroradiometer USR-40 (USHIO Inc.).

2-4. ESR measurement

The measurements were carried out at the X-band using a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 10.0 mW. The magnetic field was calibrated using 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as standard. Catalyst (20 mg) was placed in a quartz ESR tube, and the tube was evacuated at 423 K for 3 h and cooled to room temperature. O₂ (20 Torr) was introduced to the tube and kept for 10 min. The tube was photoirradiated at 298 K using a Xe lamp at λ >450 nm. The tube was then evacuated for 10 min to remove the excess amount of O₂ and analyzed at 77 K.

2-5. Analysis

Total amount of Pt in the catalysts was analyzed by an inductively-coupled argon plasma atomic emission spectrometer (ICAP-AES; SII Nanotechnology, SPS 7800), after dissolution of catalysts in an
aqua regia. TEM observations were carried out using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV. XPS analysis was performed using a JEOL JPS-9000MX spectrometer with Mg Kα radiation as the energy source. Diffuse reflectance UV-vis spectra were measured on an UV-vis spectrophotometer (Jasco Corp.; V-550 with Integrated Sphere Apparatus ISV-469) with BaSO₄ as a reference.⁶⁴

3. Results and discussion
3-1. Preparation and properties of catalysts

![Figure 6-1. (a) TEM image of Ptₓ(15%/anatase catalyst and size distribution of the Pt particles. (b) High-resolution TEM images.](image)

The Pt/TiO₂ catalysts were prepared by impregnation of Pt precursors followed by reduction with H₂,²⁶,²⁷ using anatase (Japan Reference Catalyst, JRC-TIO-1; average particle size, 21 nm; BET surface area, 81 m² g⁻¹), P25 (JRC-TIO-4; 24 nm; 57 m² g⁻¹; anatase/rutile = ca. 83/17), and rutile TiO₂ particles (JRC-TIO-6; 15 nm; 104 m² g⁻¹), supplied from the Catalyst Society of Japan. TiO₂ was added to water containing H₂PtCl₆, and the water was removed by evaporation with vigorous stirring. The resultant was calcined in air for 2 h and reduced with H₂ for 2 h at the identical temperature, affording Ptₓ/TiO₂ as brown powder. The x is the amount of Pt loaded [x (wt %) = Pt/(Pt + TiO₂) × 100], and y is the
temperature (K) for calcination and reduction treatments.

As shown in Figure 6-1a, the transmission electron microscopy (TEM) images of Pt21673/anatase catalysts exhibit monodispersed Pt particles; the average diameter of particles ($d_p$) is 3.4 nm. In addition, the high-resolution TEM images of catalysts (Figure 6-1b) reveal that the Pt particles can be indexed as $fcc$ structures, as is the case for bulk Pt (JCPDS 04-0802). Pt21673/P25 and Pt21673/rutile also contain Pt particles with similar $d_p$ (3.1 and 2.9 nm). X-ray photoelectron spectroscopy (XPS) of the catalysts shows distinctive Pt 4f peaks at 71 and 74 eV (Figure 6-2), indicating that Pt atoms exist as metallic state.28 As shown in Figure 6-3a, diffuse reflectance UV-vis spectra of the catalysts containing 2 wt % Pt exhibit broad absorption band at $\lambda >400$ nm, assigned to the intraband and interband transitions of Pt particles.29 Their absorption intensities are much lower than those of Au particles on the Au21P25 catalyst containing 2 wt % Au.19

![Figure 6-2. XPS chart for Pt/TiO$_2$ catalysts.](image-url)
Figure 6-3. (a) Diffuse reflectance UV-vis spectra of catalysts. (b) Action spectra for photocatalytic oxidation of 1 on (black) Pt\textsubscript{2673}/anatase and (white) Au\textsubscript{2}/P25 catalysts. The apparent quantum yield for the 2 formation was calculated with the following equation: \( \Phi_{AQY} \) (%) = \( \{(Y_{\text{vis}}-Y_{\text{dark}}) \times 2\}/(\text{photon number entered into the reaction vessel}) \) × 100, where \( Y_{\text{vis}} \) and \( Y_{\text{dark}} \) are the amounts of 2 formed (\( \mu \)mol) under light irradiation and dark conditions, respectively.

3-2. Catalytic activity

The activity of Pt/TiO\textsubscript{2} catalysts was studied by oxidation of benzyl alcohol (1) to benzaldehyde (2), a typical aerobic oxidation.\textsuperscript{30} The reactions were performed by stirring a toluene solution (5 mL) containing 1 (0.1 mmol) and catalyst (5 mg) under O\textsubscript{2} atmosphere (1 atm). The temperature of solution was kept rigorously at 298 ± 0.5 K. Figure 6-4 summarizes the amount of 2 produced by 12 h reaction in the dark (black bars) or visible light irradiation by a Xe lamp (\( \lambda > 450 \) nm, white bars). It is noted that both reactions selectively produced 2 (mass balance: >99%). With bare anatase TiO\textsubscript{2}, almost no reaction occurred in the dark, and visible light irradiation produced only 2 \( \mu \)mol 2. In contrast, the dark reaction with Pt\textsubscript{2673}/anatase produced 12 \( \mu \)mol 2 due to the high catalytic activity of Pt particles for aerobic oxidation.\textsuperscript{31-33} Light irradiation further enhanced the reaction; twice amount of 2 (25 \( \mu \)mol) was produced. This suggests that visible light irradiation of Pt/anatase catalyst indeed enhances aerobic oxidation.\textsuperscript{34} It is noted that the activity of Pt/anatase catalyst is much higher than that of Au\textsubscript{2}/P25 catalyst;\textsuperscript{19} Au\textsubscript{2}/P25 produced only 7.8 \( \mu \)mol 2 even under photoirradiation. Zhai et al.\textsuperscript{25} reported that
Pt/TiO₂ catalyst promotes oxidation of alcohols by visible light (λ >420 nm) under N₂ atmosphere; however, as shown in Figure 6-4, photoirradiation of Pt₂673/anatase under N₂ produced very small amount of aldehyde. This indicates that aerobic oxidation is much more efficient for alcohol oxidation.

![Catalyst Promotion of Oxidation](image)

Figure 6-4. The amount of 2 formed during aerobic oxidation of 1 with respective catalysts, (black) in the dark or (white) visible light irradiation (λ >450 nm; light intensity at 450–800 nm, 16.8 mW cm⁻²). The data obtained under N₂ (1 atm) condition were also shown in the figure. Average diameter of metal particles on the catalysts is denoted in the parenthesis. The detection limit of 2 is 0.02 μmol (4 μM) and the range of calibration is 0.004–20 mM.

Semiconductor support is necessary for the reaction enhancement by visible light irradiation. As shown in Figure 6-4, Pt₂673/SiO₂ catalyst with SiO₂ support (Aldrich; average particle size, 16 nm; BET surface area, 625 m² g⁻¹) shows almost no reaction enhancement even by photoirradiation. Visible light irradiation of Pt₂673/P25 also enhances the reaction, but the enhancement is lower than that of Pt₂673/anatase. In addition, Pt₂673/rutile is almost inactive for reaction. As shown in Figure 6-5, other anatase TiO₂ loaded with Pt particles also enhance aerobic oxidation under visible light irradiation. These data clearly suggest that Pt particles loaded on anatase TiO₂ promote efficient aerobic oxidation
under visible light. As shown in Figure 6-6, the Pt/anatase catalyst maintains its activity even after prolonged photoirradiation (~36 h), indicating that the catalyst is stable under photoirradiation.

![chemical reaction](image)

**Figure 6-5.** The amount of 2 formed during aerobic oxidation of 1 with various anatase TiO₂ catalysts loaded with Pt particles, (black) in the dark or (white) under visible light irradiation (λ >450 nm). The reaction conditions are identical to those in Figure 3 in the manuscript.
Figure 6-6. Time-dependent change in the amount of 2 formed during aerobic oxidation of 1 with respective catalysts in the dark or under visible light irradiation (λ >450 nm). The reaction conditions are identical to those in Figure 3 in the manuscript.

3-3. Electron transfer at the Pt/anatase heterojunction

The enhanced aerobic oxidation on the Pt/anatase catalyst under visible light is initiated by the intraband or interband transition of Pt particles. Some literatures\textsuperscript{35,36} reported that Pt/TiO\textsubscript{2} promotes photocatalytic reaction under visible light (λ >400 nm), although TiO\textsubscript{2} itself scarcely absorbs light at this wavelength range. This was explained by the narrowed bandgap of TiO\textsubscript{2} by the Pt loadings. In the present case, as shown in Figure 6-3b, the action spectrum analysis revealed that the absorption band of Pt\textsubscript{2(673)/anatase} correlates well with the apparent quantum yield (ΦAQY) for photocatalytic oxidation of 1 (black circle). This data clearly suggests that the enhanced aerobic oxidation on the Pt/anatase catalyst is triggered by the activation of Pt particles. It is also noted that ΦAQY for Pt\textsubscript{2(673)/anatase} is higher than that for Au\textsubscript{2}/P25 (white circle)\textsuperscript{19} at the broad wavelength range of incident light, especially at λ <600 nm. The ΦAQY values for Pt\textsubscript{2(673)/anatase} at 450 nm and 550 nm are 13.7% and 7.1%, respectively, which are much higher than those for Au\textsubscript{2}/P25 (2.9% and 3.8%).

In the Pt/anatase system, photoactivated Pt particles transfer e\textsuperscript{-} to anatase, and the e\textsuperscript{-} reduces O\textsubscript{2} on its surface. This is confirmed by ESR analysis of the catalysts at 77 K, after treatment of the sample with O\textsubscript{2} at room temperature in the dark or visible light irradiation (λ >450 nm). As shown in Figure 6-7 (blue), bare anatase TiO\textsubscript{2} treated with O\textsubscript{2} in the dark shows weak signals (g = 2.029, 2.001), which are assigned to O\textsuperscript{-} formed via a dissociative adsorption of O\textsubscript{2} onto the oxygen vacancy sites of TiO\textsubscript{2} surface.\textsuperscript{37,38} Photoirradiation of this sample does not create any new signal (Figure 6-7a, black). As
shown in Figure 6-7b, Pt\textsubscript{2(673)/anatase} treated with O\textsubscript{2} in the dark also shows O\textsuperscript{2-} signal, but photoirradiation creates strong signals assigned to a superoxide-type oxygen anion (O\textsubscript{2-}; \(g_{xx} = 2.002, g_{yy} = 2.009, g_{zz} = 2.028\)), which is stabilized on TiO\textsubscript{2} surface.\textsuperscript{39} This suggests that photoactivated Pt particles indeed transfers e\textsuperscript{-} to anatase and promotes the reduction of O\textsubscript{2} on its surface. As shown in Figure 6-7c and d, photoirradiation of Pt\textsubscript{2(673)/P25} and Pt\textsubscript{2(673)/rutile} samples creates much weaker O\textsubscript{2-} signals. This means that the O\textsubscript{2} reduction does not occur efficiently on these catalysts, and the data agree with their photocatalytic activities (Figure 6-4). It is noted that, as shown in Figure 6-7b (green), the Pt/anatase catalyst, when treated with O\textsubscript{2} at high temperature (353 K) in the dark, does not create O\textsubscript{2-} signal. This indicates that photo-thermal conversion\textsuperscript{40} on the Pt particles, even if occurs in the present system,\textsuperscript{41-44} does not promote O\textsubscript{2} reduction. This again suggests that electronic excitation of Pt particles by visible light enables e\textsuperscript{-} transfer to anatase and promotes O\textsubscript{2} reduction.

\begin{figure}[h]
\begin{center}
\includegraphics[width=\textwidth]{figure6-7.png}
\end{center}
\caption{ESR spectra of respective catalysts. The catalysts were treated with 20 Torr O\textsubscript{2}, (blue) in the dark at 298 K, (black) under visible light irradiation at 298 K, or (green) in the dark at 353 K. After evacuation, the samples were measured at 77 K.}
\end{figure}
In the Au/P25 system,\textsuperscript{19} photoactivated Au particles scarcely transfer e\textsuperscript{−} to anatase. However, in the Pt/anatase system, the Pt→anatase e\textsuperscript{−} transfer occurs successfully. This is probably due to the strong affinity between Pt particles and anatase surface. Gong et al.\textsuperscript{45} studied the adsorption properties of Pt and Au clusters onto the anatase (101) surface by means of scanning tunneling microscopy and \textit{ab initio} calculations. They clarified that Pt clusters are strongly adsorbed onto the anatase surface via the association with the steps, terraces, and oxygen vacancy sites, and the adsorption energy for Pt/anatase is ten-fold higher than that for Au/anatase. The strong Pt/anatase interaction, therefore, probably enables the Pt→anatase e\textsuperscript{−} transfer.

As shown in Figure 6-7b, photoirradiation of Pt\textsubscript{267}/anatase with O\textsubscript{2} produces superoxide-type oxygen anion (O\textsubscript{2}\textsuperscript{−}). In contrast, Au\textsubscript{2}/P25\textsuperscript{19} (Figure 6-7f) generates peroxide-type oxygen anion (O–O\textsuperscript{−}; \(g_{xx} = 2.002, g_{yy} = 2.004, g_{zz} = 2.008\)), associated with the residual positive charge on Au particles.\textsuperscript{46} The formation of O\textsubscript{2}\textsuperscript{−} species on Pt/anatase is explained by the high e\textsuperscript{−} diffusivity in the anatase conduction band. Sun et al.\textsuperscript{47} reported that the e\textsuperscript{−} diffusivity in anatase is two-fold higher than that in rutile. This may allow smooth e\textsuperscript{−} diffusion in anatase and promote O\textsubscript{2} reduction at the surface spatially separated from the Pt particles (Figure 6-7b). In contrast, on Au/P25, the Au→rutile→anatase multistep e\textsuperscript{−} transfers (Scheme 6-1) suppress smooth e\textsuperscript{−} diffusion and promote O\textsubscript{2} reduction at the surface near to the Au particles. This thus produces O–O\textsuperscript{−} species associated with the residual positive charge on Au particles (Figure 6-7f).

Mechanism for photocatalytic reaction on Pt/anatase can be depicted as Scheme 2B, similar to the mechanism in the dark (Scheme 6-2A). It is considered that the dark reaction is initiated by activation of O\textsubscript{2} on the anionic site of metal particles.\textsuperscript{20} The activated species removes H atom of alcohol and produces hydroperoxide and alcoholate species on the Pt surface.\textsuperscript{48} Subsequent removal of H atom from the species affords the product. In the photocatalytic reaction (Scheme 6-2B), photoactivated Pt particles transfer e\textsuperscript{−} to anatase (a). The e\textsuperscript{−} reduces O\textsubscript{2} and produces O\textsubscript{2}\textsuperscript{−} species (b). The O\textsubscript{2}\textsuperscript{−} species attracts H atom of alcohol and produces the hydroperoxide and alcoholate species (c). These species give rise to the product (d). These mechanisms suggest that both dark and photocatalytic reactions are initiated by the activation of O\textsubscript{2}, leading to the formation of hydroperoxide and alcoholate species. Although it is unclear whether the dark and photocatalytic reactions affect each other, the O\textsubscript{2} reduction on anatase surface promoted by e\textsuperscript{−} transfer from photoactivated Pt particles is the crucial step facilitating efficient aerobic oxidation.

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Scheme 6-2. Proposed Mechanism for Aerobic Oxidation of Alcohol on the Pt/anatase Catalyst under (A) Dark and (B) Visible Light Irradiation Conditions.

3-4. Effect of Pt amount

Photocatalytic activity of Pt/anatase catalysts depends on the amount of Pt loaded. This is confirmed by the reaction using Pt_{4(673)}/anatase catalysts with different Pt loadings \([x \text{ (wt %)}] = \text{Pt}/(\text{Pt + TiO}_2) \times 100\]. As shown in Figure 6-8a (orange), \(d_p\) of the catalysts are similar (3.3–3.4 nm). In contrast, as shown in Figure 6-9a, absorbance of the catalysts in the visible region increases with the Pt loadings due to the increase in the number of Pt particles. The bar graphs in Figure 6-8a show the results for aerobic oxidation of 1 obtained with respective catalysts. The dark activity (black bar) increases with the Pt loadings due to the increase in the number of surface Pt atoms that are active for aerobic oxidation. Visible light irradiation (white bar) further enhances the reaction, but the enhancement depends on the Pt loadings; 2 wt % Pt shows the largest enhancement, and higher loading catalysts are ineffective despite their stronger absorbance. As schematically shown in Scheme 6-3, the metal/semiconductor heterojunction creates a Schottky barrier \((\phi_h)\). Visible light irradiation leads to a collective oscillation...
of sp band or d band electrons on the metal particles and promotes the intraband or interband excitation to the sp-conduction band. This provides energy to the electrons to overcome $\phi_B$ and facilitates e\textsuperscript{−} transfer to semiconductor conduction band.\textsuperscript{50,51} The height of $\phi_B$, therefore, strongly affects the e\textsuperscript{−} transfer efficiency. As reported,\textsuperscript{52} the increase in the amount of metal loaded onto the semiconductor leads to an increase in $\phi_B$, due to the decrease in Fermi level of semiconductor. The decreased photocatalytic activity for larger Pt loading catalysts (Figure 6-8a) is therefore probably because the increased $\phi_B$ suppresses e\textsuperscript{−} transfer from photoactivated Pt particles to anatase.

**Figure 6-8.** The amount of 2 formed during aerobic oxidation of 1 with (a) Pt\textsubscript{473/y'anatase} and (b) Pt\textsubscript{773/y'anatase} catalysts in the dark or under visible light irradiation. Orange keys denote $d_{Pt}$ of catalysts. The reaction conditions are identical to those in Figure 6-3.
Figure 6-9. Diffuse reflectance UV-vis spectra of (a) Pt$_{x(673)}$/anatase and (b) Pt$_{2y}$/anatase catalysts.

Scheme 6-3. Proposed Mechanism for Electron Transfer from the Photoactivated Pt Particles to Anatase. $E_{\text{vac}}$, $E_F$, $W_{\text{Pt}}$, $\phi_B$, and $\chi$ denote the vacuum level, Fermi level, work function of Pt, Schottky barrier height ($= W_{\text{Pt}} - \chi$), and electron affinity of anatase conduction band, respectively.
3-5. Effect of Pt particle size

The size of Pt particles also affects the photocatalytic activity. To clarify this, the Pt_{2\theta}/anatase catalysts with 2 wt % Pt were prepared at different calcination and reduction temperature, y (K). As shown in Figure 6-8b (orange), $d_\text{Pt}$ of the catalysts increase with the temperature increase due to the sintering of Pt particles; $d_\text{Pt}$ for Pt_{2\theta=473}, Pt_{2\theta=573}, Pt_{2\theta=673}, and Pt_{2\theta=823} catalysts are 2.1, 2.5, 3.4, 5.0, 39.1, and 52.8 nm, respectively. X-ray diffraction patterns of the catalysts indicate that the anatase-to-rutile phase transition scarcely occurs (Figure 6-10). As shown by the black bars in Figure 6-8b, in the dark condition, the Pt_{2\theta=673} catalyst shows the highest activity, and the catalysts with smaller or larger Pt particles show decreased activity. The low activity of smaller Pt particles is due to the decreased density of low-coordination Pt sites that are active for oxidation.\(^{33}\) In contrast, larger Pt particles contain decreased number of surface Pt atoms and, hence, show decreased activity.\(^{30}\)

![Figure 6-10. XRD patterns of Pt_{2\theta}/anatase catalysts. The measurements were performed on a Philips XXX diffractometer with Cu Kα radiation.](image)

As shown by the white bars in Figure 6-8b, the photocatalytic activity of Pt_{2\theta}/anatase shows $d_\text{Pt}$ dependence similar to the dark activity. The Pt_{2\theta=673} catalyst shows the highest activity, and the catalysts with smaller or larger Pt particles show decreased activity. As shown in Figure 6-9b, absorbance of the catalysts in the visible region is similar, although their $d_\text{Pt}$ are different (Figure 6-8b). This indicates that
the light absorption efficiencies for these catalysts are similar. The low photocatalytic activity of the catalysts with smaller Pt particles is due to the higher $\phi_p$ created at the Pt/anatase heterojunction. As reported,\textsuperscript{54} the work function of metal particles ($W_m$) increases with a decrease in their particle size and is expressed by the following equation:

$$W_M (eV) = W_{M,\infty} + \frac{1.08}{d_M}$$

$W_{M,\infty}$ and $d_M$ are the work function of planar metal and the diameter of metal particles, respectively. $W_{M,\infty}$ is 5.65 eV,\textsuperscript{55} and $W_p$ for Pt particles on the Pt\textsubscript{(473)}, Pt\textsubscript{(573)}, Pt\textsubscript{(673)}, Pt\textsubscript{(773)}, Pt\textsubscript{(2823)}, and Pt\textsubscript{(873)} catalysts are determined using their $d_p$ values to be 6.16, 6.08, 5.97, 5.87, 5.68, and 5.67 eV, respectively. As summarized in Figure 6-11 (black), $W_p$ for Pt particles indeed becomes more positive with a decrease in the particle size. As shown in Scheme 6-3, $\phi_p$ is defined as the difference between the work function of Pt particles and the electron affinity of anatase $E_{CB}$ ($\phi_p = W_p - \chi$).\textsuperscript{56} This suggests that the catalysts with smaller Pt particles create higher $\phi_p$. This may suppress smooth $e^-$ transfer from the photoactivated Pt particles to anatase, resulting in lower photocatalytic activity (Figure 6-8b).

![Figure 6-11](image)

**Figure 6-11.** The work function of Pt particles ($W_p$) and the number of perimeter Pt atoms ($N_{perimeter}$) for Pt\textsubscript{2823}/anatase catalysts, determined with the eqs. 1–5 using $d_p$ values. The detailed calculation results are shown in Table 6-1.
Table 6-1. Calculation details for the number of perimeter Pt atoms on Pt\textsubscript{210/1}anatase catalysts.

<table>
<thead>
<tr>
<th>( y / \text{K} )</th>
<th>( d_{\text{Pt}} )</th>
<th>( N_{\text{total}} )</th>
<th>( m )</th>
<th>( N_{\text{perimeter}} )</th>
<th>( N_{\text{particle}} )</th>
<th>( N_{\text{perimeter}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( / \text{nm} )</td>
<td>( / - )</td>
<td>( / - )</td>
<td>( / \text{-} )</td>
<td>( / \mu\text{mol g}^{-1} )</td>
<td>( / \mu\text{mol g}^{-1} )</td>
</tr>
<tr>
<td>473</td>
<td>2.1 ± 0.4</td>
<td>319 ± 10</td>
<td>5.1 ± 0.1</td>
<td>12.2 ± 0.1</td>
<td>(3.21 ± 0.11) ( \times 10^{-1} )</td>
<td>3.9 ± 0.1</td>
</tr>
<tr>
<td>573</td>
<td>2.5 ± 0.4</td>
<td>539 ± 14</td>
<td>5.9 ± 0.1</td>
<td>14.8 ± 0.1</td>
<td>(1.90 ± 0.05) ( \times 10^{-1} )</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>673</td>
<td>3.4 ± 0.6</td>
<td>(136 ± 7)</td>
<td>7.9 ± 0.2</td>
<td>20.7 ± 0.4</td>
<td>(7.6 ± 2.1) ( \times 10^{-2} )</td>
<td>1.6 ± 0.1</td>
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<tr>
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<td>( \times 10^1 )</td>
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<td></td>
</tr>
<tr>
<td>773</td>
<td>5.0 ± 3.2</td>
<td>(431 ± 270)</td>
<td>11.4 ± 0.4</td>
<td>31.2 ± 1.3</td>
<td>(2.4 ± 0.9) ( \times 10^{-2} )</td>
<td>(7.4 ± 0.9) ( \times 10^{-1} )</td>
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<td>( \times 10^1 )</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>823</td>
<td>39.1 ± 14.3</td>
<td>(206 ± 26)</td>
<td>85.7 ± 2.5</td>
<td>254 ± 8</td>
<td>(5.0 ± 2.3) ( \times 10^{-5} )</td>
<td>(1.3 ± 0.2) ( \times 10^{-2} )</td>
</tr>
<tr>
<td></td>
<td>( \times 10^4 )</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>873</td>
<td>52.8 ± 15.5</td>
<td>(508 ± 50)</td>
<td>116 ± 3</td>
<td>344 ± 10</td>
<td>(2.0 ± 1.1) ( \times 10^{-5} )</td>
<td>(6.9 ± 1.0) ( \times 10^{-3} )</td>
</tr>
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<td>( \times 10^4 )</td>
<td></td>
<td></td>
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</tbody>
</table>

\( a \) Average diameter of Pt particles determined by TEM observations. \( b \) The number of total Pt atoms per particle. \( c \) The number of shells. \( d \) The number of perimeter Pt atoms per particle. \( e \) The number of Pt particles per gram catalyst. \( f \) The number of perimeter Pt atoms per gram catalyst.

Scheme 6-4. Relationship between the Pt Particle Size and the Number of Perimeter Pt Atoms for Pt\textsubscript{210/1}anatase. The calculation details for \( N_{\text{perimeter}} \) are summarized in Table 6-1.
In contrast, larger Pt particles create lower $\phi_p$ due to their lower $W_{Pt}$; therefore, the e⁻ transfer to anatase would occur more easily. However, as shown in Figure 6-8b, photocatalytic activity of the catalysts with larger Pt particles is much lower than that of Pt_2(673). As shown in Scheme 6-4, the e⁻ transfer from photoactivated Pt particles to anatase occurs through the perimeter Pt atoms indicated by the blue spheres and, hence, the number of perimeter Pt atoms may affect the e⁻ transfer efficiency. As shown in Figure 6-1b, the high-resolution TEM images of catalysts revealed that the shape of Pt particles is a part of cuboctahedron, which is surrounded by (111) and (100) surfaces. The Pt particles on anatase surface therefore can simply be modeled as a fcc cuboctahedron, as often used for related systems.\(^{58,59}\) This thus allows rough determination of the number of perimeter Pt atoms. Considering the full shell close packing cuboctahedron for Pt particle where one Pt atom is surrounded by twelve others, the number of total Pt atoms per particle ($N_{total*}$) can be expressed by eq. 2 using the number of shells ($m$). $N_{total*}$ is rewritten with the average diameter of Pt particle ($d_{Pt}$) and the atomic diameter of Pt [$d_{atom,pt}$ (=0.278 nm)].\(^{60}\) The number of perimeter Pt atoms per particle ($N_{perimeter*}$) is expressed by eq. 3.\(^{57}\)

\[
N_{total*} (-) = \frac{10m^3 - 15m^2 + 11m - 3}{3} = \left( \frac{d_{Pt}}{1.105 \times d_{atom,pt}} \right)^3
\]

\[
N_{perimeter*} (-) = 3m - 3
\]

The number of Pt particles per gram catalyst ($N_{particle}$) is expressed by eq. 4, using the percent amount of Pt loaded onto the catalyst [$x$ (wt %)], molecular weight of Pt [$M_w$ (= 195.1 g mol⁻¹)], and $N_{total*}$. The number of perimeter Pt atoms per gram catalyst ($N_{perimeter}$) is therefore expressed by eq. 5.

\[
N_{particle} (\text{mol g}^{-1}) = \frac{x}{100 \times M_w \times N_{total*}}
\]

\[
N_{perimeter} (\text{mol g}^{-1}) = N_{perimeter*} \times N_{particle}
\]

The $N_{perimeter}$ values for respective Pt(24)/anatase catalysts can therefore be calculated using their $d_{Pt}$ determined by the TEM observations (Table 6-1). As shown in Figure 6-11 (white), the $N_{perimeter}$ values decrease with an increase in the Pt particle size; the value for Pt_2(673) is 3.9 μmol g⁻¹, but that for Pt_2(873) is only 6.9 × 10⁻³ μmol g⁻¹. This suggests that the particle size increase leads to significant decrease in $N_{perimeter}$. As shown in Figure 6-7e, ESR analysis of the Pt_2(873) catalyst after treatment with O₂ under visible light irradiation shows O₂⁻ signal much weaker than that of Pt_2(673) (Figure 6-7b). This indicates that the catalysts with larger Pt particles are indeed inefficient for e⁻ transfer to anatase, although their $\phi_p$ values are lower. These findings clearly suggest that the decreased number of perimeter Pt atoms
Table 6-2. Effect of Sunlight Exposure on Aerobic Oxidation of Alcohols with Pt and Au Catalysts.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Sunlight\textsuperscript{b}</th>
<th>Conversion \textsuperscript{c}</th>
<th>Product</th>
<th>Yield \textsuperscript{d}</th>
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<tr>
<td>1</td>
<td></td>
<td>Pt\textsubscript{2673} anatase</td>
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<td>75</td>
<td></td>
<td>72</td>
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<td>2</td>
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<td>3</td>
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<td>80</td>
</tr>
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<td></td>
<td>59</td>
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<td>Au\textsubscript{2}/P25</td>
<td>+</td>
<td>49</td>
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\textsuperscript{a} Reaction conditions: toluene (5 mL), alcohol (25 \textmu mol), catalyst (5 mg), O\textsubscript{2} (1 atm), exposure time (4 h). The average light intensity at 300–800 nm was 8.1 mW cm\textsuperscript{-2}, which involves \lambda < 400 nm light with only ca. 2%. The solution temperature during exposure was 288–293 K. \textsuperscript{b} The dark reaction (−) was performed at 293 K. \textsuperscript{c} = (alcohol converted) / (initial amount of alcohol) x 100. \textsuperscript{d} = (product formed) / (initial amount of alcohol) x 100.

suppresses e\textsuperscript{−} transfer from photoactivated Pt particles to anatase and results in lower photocatalytic activity. As shown in Figure 6-8b, the Pt\textsubscript{2673}, Pt\textsubscript{2673}, and Pt\textsubscript{2773} catalysts contain Pt particles with similar sizes (2–5 nm), but the Pt\textsubscript{2673} catalyst shows the highest photocatalytic activity. This means that, as shown in Figure 6-11, the Pt particle size strongly affects W\textsubscript{Pt} and N\textsubscript{perimeter}, and this trade-off relationship is critical for the activity of photocatalysis. As summarized in Scheme 6-4, the 3–4 nm Pt
particles with shell number 7–10, create relatively low $\phi_B$ and relatively large number of perimeter Pt atoms at the Pt/anatase heterojunction and, hence, act as highly active photocatalysts.

The Pt$\text{_{2673}}$/anatase catalyst successfully promotes aerobic oxidation of alcohols under sunlight irradiation at ambient temperature. Table 6-2 summarizes the results for oxidation of various alcohols obtained with Pt$\text{_{2673}}$/anatase catalyst under sunlight exposure, where the temperature of solution during reaction was 288–293 K. Sunlight exposure selectively oxidizes alcohols to the corresponding carbonyl compounds with very high yields (72–99%). These yields are much higher than those obtained with Pt$\text{_{2673}}$/anatase in the dark at 293 K or with the Au$_2$/P25 catalyst$^{19}$ under sunlight exposure. These data suggest that the Pt/anatase catalyst is successfully activated by sunlight and acts as efficient photocatalyst.

4. Conclusion

We found that Pt nanoparticles loaded on anatase TiO$_2$ behave as highly efficient photocatalysts driven by visible light irradiation. The high photocatalytic activity of this system is due to the smooth $e^-$ transfer from photoactivated Pt particles to anatase. This promotes efficient O$_2$ reduction on the anatase surface and facilitates charge separation at the Pt/anatase interface. The activity of this photocatalysis depends on the height of Schottky barrier and the number of perimeter Pt atoms. The catalyst with 2 wt % Pt, containing 3–4 nm Pt nanoparticles, facilitates efficient $e^-$ transfer from the photoactivated Pt particles to anatase and shows the highest photocatalytic activity. Sunlight activation of the catalyst successfully promotes selective and efficient oxidation of alcohols. The efficient charge separation at the Pt/anatase heterojunction clarified here may contribute to the development of more active catalysts and the design of photocatalytic systems for selective organic transformations by sunlight.

5. References


The amount of 2 formed is proportional to the intensity of incident light. Photoreaction of 1 was performed with different light intensity by changing the distance from the light source to the samples. The amount of 2 formed by 12 h photoirradiation was 25 μmol (16.8 mW cm⁻²), 35 μmol (38.0 mW cm⁻²), and 45 μmol (54.9 mW cm⁻²), respectively.


Photo-thermal conversion on the photoirradiated Pt particles scarcely occurs in the present system. The temperature increase on the surface of an individual Pt particle in solution under photoirradiation can roughly be estimated by the equation, \( \Delta T = \sigma_{abs} I / (4\pi R_{eq} \beta \kappa) \), where \( \sigma_{abs} \) = absorption cross section, \( I \) = intensity of the incident light, \( R_{eq} \) = radius of a sphere with the same volume as the particle, \( \beta \) = thermal capacitance coefficient dependent on nanoparticle aspect ratio, \( \kappa \) = thermal conductivity of solvent (ref 42). The \( \sigma_{abs} \) value for <100 nm Pt particles is reported to be \( <1 \times 10^{-14} \text{ m}^2 \) (ref 43). Other parameters for our catalysts are: \( R_{eq} <30 \text{ nm}, I = 168 \text{ W m}^{-2}, \beta = 1, \kappa = 0.13 \text{ W m}^{-1} \text{ K}^{-1} \) (ref 44). The theoretical temperature increase, \( \Delta T \), is determined with these parameters to be \( 3.4 \times 10^{-5} \text{ K} \). This very small temperature increase suggests that photo-thermal conversion scarcely occur in the present Pt/anatase system.


General Conclusions

This dissertation work described selective organic transformations by semiconductor photocatalysts loaded with Pt and Pd nanoparticles to achieve "photocatalytic organic synthesis". In the first four chapters (I-IV), photocatalytic activation of substrates by UV light irradiation was described. In the two other chapters (V and VI), the author described the photocatalytic activation of substrates by visible light irradiation.

In Chapter I, the author found that a new strategy for the acid- and oxidant-free synthesis of benzimidazoles using o-arylenediamines and alcohols as the reactants at room temperature under UV light irradiation condition (λ > 300 nm). This process employs nanoparticles that comprise a titanium dioxide (TiO₂) semiconductor loaded with Pt nanoparticles. This is promoted by one-pot multiple catalytic transformations on Pt/TiO₂, which involve a platinum-assisted photocatalytic oxidation of alcohols on TiO₂ and a catalytic dehydrogenation on the surface of the platinum particles. The amount and size of platinum particles are important factors. The catalyst containing 0.2 wt% Pt, with a relatively large amount of Pt atoms and a small Pt particle size (<4 nm), exhibits the highest activity and selectivity. This process has significant advantages when compared with other methods: (i) a cheap and stable reactant (alcohol), (ii) it does not require the use of acids or oxidants, (iii) the by-products formed are harmless (only water and molecular hydrogen form during the reaction), and (iv) the reaction proceeds under milder ambient conditions. Therefore, this process has the potential to enable a more sustainable benzimidazole synthesis.

In Chapter II, TiO₂ loaded with Pd nanoparticles were used as catalysts for photocatalytic hydrodenitrogenation of aromatic cyanide in ethanol as a hydrogen source. These catalysts promote denitrogenation and produce toluene derivatives and triethylamine with very high selectivity under UV light (λ > 300 nm) irradiation at room temperature. Photoexcited Pd/TiO₂ catalysts produce acetaldehyde and the active H-Pd species. Consecutive reactions involving the hydrogenation by H-Pd species and the condensation with aldehyde facilitate efficient hydrodenitrogenation of aromatic cyanides. The amount of Pd loaded and the size of Pd particles strongly affect the denitrogenation activity. The Pd/TiO₂ catalyst with a relatively low Schottky barrier height at the Pd/TiO₂ heterojunction and a large number of surface Pd atoms is necessary for efficient denitrogenation.

In Chapter III, the author found that Pd/TiO₂ catalyst promotes N-monoalkylation of primary amine with alcohol under UV light irradiation (λ > 300 nm) at room temperature. Several kinds of secondary amines are successfully produced with high yields. Tandem photocatalytic and catalytic reactions
promote three consecutive reactions, consisting of Pd-assisted alcohol oxidation on the photoactivated TiO₂, catalytic condensation of the formed aldehydes with amines on the TiO₂ surface, and hydrogenation of formed imine with H atoms on the Pd particles. The rate-determining step is the imine hydrogenation via an adsorption of imine on Pd surface. The imine adsorption onto the larger triangle site is strongly suppressed by competitive adsorption of alcohol. As a result of this, the catalyst with 2-2.5 nm Pd particles, which contain relatively larger number of triangular Pd atoms and do not promote strong alcohol adsorption, shows the highest activity for imine hydrogenation and promotes efficient N-alkylation. This tandem catalytic system offers significant advantages: (i) no harmful byproduct forms; (ii) the reaction proceeds at room temperature; and (iii) several secondary amines are successfully produced. The tandem reaction promoted by photocatalytic and catalytic action, therefore, have a potential to be a powerful method for one-pot synthesis of organic compounds in an environmentally-friendly way.

In Chapter IV, the author found that UV irradiation (λ >300 nm) of TiO₂ loaded with Pd-Pt alloy promotes efficient dehalogenation of organic halides with alcohol. The activity is more than three times that of TiO₂ loaded with Pd nanoparticles and higher than the conventional method with molecular hydrogen. Photoexcited catalysts produce carbonyl compounds and H⁺, whereas the photoformed e⁻ reduces H⁺ on the Pt site. Sequentially, the formed H atom transfers to the adjacent Pd site and promotes dehalogenation. This high activity is due to the enhanced consumption of photoformed e⁻ on the Pt site by H⁺ reduction and sequential efficient transfer of the formed hydrogen atom to the adjacent Pd site within the alloy particles. This offers crucial advantages: (i) safe alcohols can be used as a hydrogen source; and, (ii) the reaction proceeds much faster. Therefore, this Pd-Pt bimetallic alloy system has a potential to proceed a Pd-based hydrogenation process.

In Chapter V, tungsten trioxide (WO₃) loaded Pt nanoparticles (Pt/WO₃) were used as catalysts for oxidation of cyclohexane (CHA) with molecular oxygen (O₂) under visible light irradiation (λ >420 nm). These catalysts successfully promote partial oxidation of CHA to produce cyclohexanol (CHA-ol) and cyclohexanone (CHA-one) with ca. 93% selectivity. The ESR measurement with a spin trapping reagent and the photocatalytic reaction with a superoxide radical (O₂⁻) scavenger indicate that the high selectivity for CHA oxidation on Pt/WO₃ is because subsequent photocatalytic decomposition of CHA-ol and CHA-one is suppressed. In the Pt/WO₃ system, the photoformed electrons on the conduction band of WO₃ are consumed by a multi-electron reduction of O₂ on the Pt particles (formation of H₂O and H₂O₂), where a single-electron reduction of O₂ is unfavored. This suppresses the formation of O₂⁻ that promotes decomposition of CHA-ol and CHA-one and, hence, results in selective formation
of these products.

In Chapter VI, the author found that Pt nanoparticles loaded on anatase TiO$_2$ behave as highly efficient photocatalysts driven by visible light irradiation ($\lambda > 450$ nm). The high photocatalytic activity of this system is due to the smooth $e^-$ transfer from photoactivated Pt particles to anatase. This promotes efficient O$_2$ reduction on the anatase surface and facilitates charge separation at the Pt/anatase interface. The activity of this photocatalysis depends on the height of Schottky barrier and the number of perimeter Pt atoms. The catalyst with 2 wt% Pt, containing 3-4 nm Pt nanoparticles, facilitates efficient $e^-$ transfer from the photoactivated Pt particles to anatase and shows the highest photocatalytic activity. Sunlight activation of the catalyst successfully promotes selective and efficient oxidation of alcohols. The efficient charge separation at the Pt/anatase heterojunction clarified here may contribute to the development of more active catalysts and the design of photocatalytic systems for selective organic transformation by sunlight.
Suggestions for Future Work

This dissertation work described the selective organic transformations by semiconductor photocatalysts loaded with Pt and Pd nanoparticles. The author points out here the extension of this work for the design of visible light-driven photocatalysis towards the application of sunlight as a light source for organic synthesis.

Previously, our research group found that Au nanoparticles with small particle size (<5 nm) located at the interface of anatase/rutile TiO₂ particles behave as highly active sites for plasmonic catalysts under visible light.₁ In Chapter VI, by applying the Au/TiO₂ system, the author also found that Pt nanoparticles with appropriate particle size (3-4 nm) located at anatase TiO₂ particles behave as highly active sites for photocatalysts under visible light. ESR analysis clearly revealed that the heterojunction of Pt/anatase facilitates direct transfer of e⁻ from the photoactivated Pt particles to anatase TiO₂ and efficient O₂ reduction. The catalyst successfully promotes aerobic oxidation of alcohols under sunlight. In addition, on the basis of the catalyst architecture clarified from these results, the author proposes more efficient visible light-induced photocatalysts. Figure 7 shows the proposal of new catalysts: they are (1) TiO₂ loaded with Au–Cu bimetallic alloy nanoparticles, and (2) TiO₂ loaded with Pt-Cu bimetallic alloy nanoparticles.

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**Figure 7.** Suggestion for new visible light-induced photocatalyst loaded with metal nanoparticles

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1. Reference or citation needed for this previous finding.
(1) TiO$_2$ loaded with Au–Cu bimetallic alloy nanoparticles

As reported,$^3$ alloying of Au with other noble metals affects strongly on the catalytic activity. This alloy effect is probably due to the e$^-$ transfer phenomena from the metal with small electronegativity$^3$ to the metal with large electronegativity (Figure 8a). In addition, as reported,$^4$ Au-Cu alloy particles with ca. 3 nm diameter loaded on silica promotes aerobic oxidation of alcohols with 1.5-fold higher than the monometallic Au particles. The enhanced activity of Au-Cu alloy is considered to be due to the efficient activation of O$_2$ on the alloy site. These alloy particles, however, rapidly lose their activity during the reaction, because O$_2$ oxidizes the surface Cu atoms and eliminates the alloying effect.$^5$ Therefore, creation of Au-Cu alloy catalysts which enable to avoid the oxidation of surface Cu atoms by O$_2$ is necessary for highly efficient aerobic oxidation under ambient conditions. The Au–Cu bimetallic alloy nanoparticles with visible light irradiation are probably one of the new approaches to avoid the oxidation of surface Cu atoms (Figure 7a). Au-Cu alloy particles activate molecular oxygen and promote aerobic oxidation of alcohols (Figure 9a). Simultaneously, the oxidized Cu species on the surface of catalyst with visible light is reduced to Cu$^0$ by a transfer of the plasmon electrons of photoactivated Au particle to oxidized Cu species, leading to suppression of oxidation of Cu on the surface (Figure 9b). This may promote efficient aerobic oxidation of alcohols without decreasing the activity. We have already made Au–Cu bimetallic alloy particles loaded on TiO$_2$ particles, with ca. 2.5 nm diameter and shows enhanced photocatalytic activity for aerobic oxidation than Au/TiO$_2$ catalyst under visible light irradiation. Although the detailed reaction mechanisms remain to be clarified, this alloy system with visible light irradiation would be one of the candidates for the improvement of catalytic activity.

![Figure 8. Work functions of noble metals.](image-url)
Figure 9. Proposed mechanism for aerobic oxidation on AuCu/TiO_2 catalyst. (purple) gold atom, (blue) copper atom, (gray) oxidized copper atom, and (red) oxygen atom.

(2) TiO_2 loaded with Pt-Cu bimetallic alloy nanoparticles

As noted above, alloying of Au and Cu affects strongly in the catalytic activity. This is probably because visible light-induced plasmon activation of e^- on Au reduces the oxidized surface Cu atoms. As shown in Chapter VI, visible light-induced photocatalysis on Pt/TiO_2 is initiated by direct e^- injection from photoactivated Pt particles to anatase TiO_2 conduction. Therefore, Pt-Cu alloying system may also enhance the catalytic activity (Figure 7b). When the photoactivated Pt particles inject e^- to TiO_2 conduction band, the e^- have to overcome the Schottky barrier. The height of the barrier decreases with decrease of work function of metal. The work function of Pt-Cu alloying metal, therefore, becomes smaller than Pt (Figure 8b), leading to more efficient e^- transfer to TiO_2 conduction band. The authors have already made PdCu/TiO_2 catalysts and the catalyst shows very high activity for aerobic oxidation of alcohols. It must be noted that the catalytic activity is much higher than Pt/TiO_2 catalyst. Although the detailed reaction mechanisms remain to be clarified, this alloy system would also possess one of the possibilities for the improvement of catalytic activity under visible light.
References


List of Publication

Papers:


Related works:


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