PHOTOCATALYTIC OXIDATION OF GAS PHASE VOLATILE ORGANIC COMPOUNDS USING UNDOPED AND METAL IONS DOPED TITANIUM DIOXIDE THIN FILMS.

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ABSTRACT

Heterogeneous photocatalytic oxidation allows the oxidation of airborne volatile organic compounds (VOCs) into carbon dioxide and water in the presence of a semiconductor catalyst and UV light source. Titanium dioxide (TiO_2), due to its chemical stability, non-toxicity and low cost represents one of the most efficient photocatalyst. However, only the ultraviolet fraction of the solar irradiation is active in the photoexcitation processes using pure TiO_2 and although, TiO_2 can treat a wide range of VOCs, the effectiveness of the process for pollution abatement is still low. A more effective and efficient catalyst therefore must be formulated. Doping TiO_2 with metal ions was considered with the aim of improving TiO_2 photocatalytic properties. In this study transparent TiO_2 thin films were prepared using the sol-gel and dip-coating method. Various ratios of doped TiO_2 thin films were also prepared using Cr^{3+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+} and Ag^{+} ions. The photoactivity of the catalyst was evaluated by the photodegradation of VOCs, conducted in a home built glass reactor. Photocatalytic oxidation of benzene using various ratios of metal-doped TiO_2 showed an optimum dopant to metal ion ratio that indicates the dependency of TiO_2 photocatalytic reactivity on dopant concentration. Photocatalytic oxidation of benzene, toluene, *m*-xylene, acetone and tetrachloroethylene was conducted using the catalyst with the optimum ratio. It was observed that the photoactivity of doped TiO_2 substantially depends on the type and concentration of dopant and VOCs. Dopants affect the photoreactivity of TiO_2 by acting either as electron/hole trap or electron-hole recombination center. High photocatalytic degradation of all the VOCs was observed with pure TiO_2. However adding Fe^{3+} and Ag^{+} into TiO_2 increased the photodegradation of benzene and acetone while Zn^{2+} in toluene and *m*-xylene degradation. Dopants such as Cr^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Mn^{2+} decreased the photoreactivity of TiO_2 in the photodegradation of all VOCs under studied. Dopants have no effect in TeCE degradation. However, TeCE shows highest degradation compared to the non-chlorinated hydrocarbon. This observation was attributed to the participation of chlorine radical, which induced a chain reaction mechanism. Preliminary studies on the mineralization of VOCs showed that CO_2 was formed during the photooxidation process using pure or doped photocatalyst. The formation of new compounds, however, was not detected. The experimental ratio of VOCs degraded against the amount of CO_2 formed showed that the photodegradation of VOCs is a partial oxidation process. Structural and optical properties of the thin films were characterized using XRD, SEM/EDAX, XPS, UV-Vis and PL spectroscopy. All thin films showed primarily the anatase phase. However, the presence of rutile in doped TiO_2 contributed to the reduced photoreactivity of TiO_2. Surface species such as Ti^{4+}, surface hydroxyl and physically adsorbed water increased the photoreactivity of TiO_2 but Ti^{3+} reduced its activity. Dopants such as Zn^{2+}, Mn^{2+} and Ag^{+} shift the absorption edge of TiO_2 into the visible region indicating the possibility of photocatalytic process using visible light.

ABSTRAK

Pengoksidaan fotopemangkinan heterogen melibatkan pengoksidaan bahan mudah meruap (VOCs) kepada karbon dioksida dan air dengan menggunakan mangkin semikonduktor dan cahaya UL. Titanium dioksida merupakan fotomangkin yang sangat berkesan kerana kestabilan kimia, tidak toksik dan murah. Bagaimanapun, dalam pancaran solar, hanya kawasan UL adalah aktif dalam proses fotopengujaan TiO_2 tulen. Walaupun TiO_2 boleh merawat sejumlah besar VOCs, keberkesanan proses ini dalam mengawal pencemaran udara masih rendah. Oleh itu mangkin yang lebih berkesan dan cekap perlu disediakan. Kaedah mendop TiO_2 dengan ion logam telah dipertimbangkan untuk meningkatkan sifat mangkinfoto TiO_2. Dalam kajian ini saput tipis TiO_2 telah disediakan dengan menggunakan kaedah sol-gel dan celup angkat. Saput tipis dengan berbagai nisbah bahan dop juga disediakan menggunakan ion Cr^{3+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+} dan Ag^{+}. Aktiviti fotomangkin telah dinilai melalui foto degradasi sebatian mudah meruap di dalam reaktor kaca. Pengoksidaan fotomangkin benzena menggunakan semua mangkin menunjukkan satu nilai optimum bahan pendop terhadap TiO_2. Nilai ini menunjukkan bahawa aktiviti fotomangkin TiO_2 bergantung kepada kepekatan bahan pendop. Fotodegradasi benzena, toluena, *m*-silena, aseton dan tetrakloroetilena (TeCE) telah dikaji menggunakan mangkin pada nisbah yang optimum. Diperhatikan bahawa fotoaktiviti TiO_2 berpendop bergantung kepada jenis dan kepekatan pendop dan VOCs. Dopan mempengaruhi fotoreaktiviti TiO_2 dengan bertindak sebagai perangkap e^-/h^+ atau sebagai pusat pengabungan e^-/h^+. Fotodegradasi VOCs adalah tinggi menggunakan TiO_2 tulen. Tetapi penambahan Fe^{3+} dan Ag^{+} ke dalam TiO_2 meningkatkan fotoreaktiviti TiO_2 terhadap degradasi benzena dan aseton manakala Zn^{2+} untuk toluena dan *m*-silena. Dopan seperti ion Cr^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, dan Mn^{2+} menurunkan aktiviti TiO_2. Fotodegradasi TeCE bagaimanapun tidak dipengaruhi oleh dopan tetapi fotodegradsi TeCE adalah sangat tinggi berbanding sebatian hidrokarbon tanpa klorin. Ini adalah berpunca daripada penglibatan radikal klorin yang menyuntik penghasilan mekanisme rantai. Kajian awal mineralisasi VOCs menunjukkan bahawa CO_2 terbentuk semasa proses fotopengoksidaan menggunakan fotomangkin tulin atau berpendop. Pembentukkan sebatian baru, bagaimanapun, tidak dapat dikesan menggunakan GC-MS. Nisbah VOCs yang terdegradasi terhadap CO_2 yang terbentuk menunjukkan fotodegradasi VOCs adalah pengoksidaan separa. Sifat struktur dan optik saput tipis dicirikan menggunakan XRD, SEM/EDAX, XPS, UV-Vis dan PL. Semua mangkin menunjukkan fasa anatas. Kewujudan fasa rutil menyebabkan penurunan fotoaktiviti TiO_2. Spesies permukaan seperti Ti^{4+}, hidrosil dan air meningkatkan fotoaktiviti TiO_2 tetapi Ti^{3+} di dapati menurunkan kereaktifan TiO_2. Bahan pendop seperti ion Zn^{2+}, Mn^{2+} dan Ag^{+} mengubah penyerapan TiO_2 ke kawasan nampak, menunjukkan kemungkinan foto degradasi dapat dijalankan menggunakan cahaya nampak.

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List of Abbreviations/Symbols/Terms

VOCs - Volatile Organic Compounds
CB - Conduction Band
VB - Valence Band
E_{bg} - Band Gap Energy
E_g - Optical Band Gap
RF - Radio Frequency
GC - Gas Chromatography
GC-MS - Gas Chromatography – Mass Spectrometer
FID - Flame Ionization Detector
UV-Vis - Ultraviolet Visible
XRD - X-Ray Diffraction Analysis
XPS - X-Ray Photoelectron Spectroscopy
SEM - Scanning Electron Microscope
PL - Photoluminescence
EDAX - Electron Dispersive X-Ray Analysis
L-H - Langmuir – Hinshelwood
n - Refractive index
d - Film Thickness
k - Reaction Rate Constant
K - Adsorption Equilibrium Constant
α - Adsorption Coefficient
r - Degradation Rate of VOCs
t - Reaction Time (minutes)
C - Concentration of Gaseous VOCs (ppm)
R - Reflectivity
T - Transmittance

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CHAPTER 1

INTRODUCTION

1.0 Air Polltion

In recent years as more countries become a more developed and industrialized nation, the quality of our environment deteriorates dramatically. Increased human activities accompanied by rapid industrial expansion have become the main contributors to water and air pollution. Volatile organic compounds (VOCs) which are considered as the most important anthropogenic pollutants generated in urban and industrial areas (Avila, 1998) are emitted to the atmosphere through the use of petroleum, manufacturing of organic chemicals, polymers, petrochemical and allied industries (Papaefthimou, 1998). Solvent thinners, degreasers, cleaners, lubricants and liquid fuels are also sources of VOCs emitted from small industries such as dry cleaners, electronic and auto repair shops.

Motor vehicles, however, remained the major source of VOCs in the world (Walsh, 1999). In 1999 the world's vehicle population inches over 700 million. In Malaysia, about 8.9 million vehicles were registered in 1998 and it was estimated that 2 million tonnes of hydrocarbon, 38,000 tonnes of sulfur dioxide and 17,000 tonnes of particulate were released to the atmosphere (Department of Environment Malaysia, 1998). Through development, air pollution has become a major environmental concerned not only in Malaysia but the world as well.

1.1 Volatile Organic Compounds (VOCs)

The term VOCs is used to identify all compounds containing carbon and present in the atmosphere, with the exception of elemental carbon, carbon monoxide and carbon dioxide (Augugliaro, 1999). VOCs are defined as having a boiling point that ranges between 50 °C and 260 °C (Jones, 1999). Their low boiling point means that they will readily emit gas vapors into the air at ambient temperatures.

VOCs include a wide range of substances with diverse effects. The most significant problem related to VOCs is the production of photochemical oxidants, for example, ozone and peroxyacetyl nitrate (PANs) (Japer, 1991) which is implicated in the formation of acid rain (Fisherman, 1991). Emission of VOCs also contributed to localized pollution problems of toxicity and odour. Many VOCs are also implicated in the depletion of the stratospheric ozone layer and may contribute to global warming (Alberici, 1997).

Many VOCs are toxic, and some are considered *carcinogenic, mutagenic*, or *teratogenic* (Wilkinson, 1987). Exposure to VOCs can result in both acute and chronic health effects. It is possible that asthmatics and other individuals with prior respiratory complaints may be particularly susceptible to low-dose VOCs exposures (Norback, 1995). At high concentrations, many VOCs are potent narcotics, and can depress the central nervous system (Jones, 1999). Exposures can also lead to irritation of the eyes and respiratory tract and cause sensitization reactions involving the eyes, skin and lungs. The occurrence of these compounds in the atmosphere therefore posed a greater threat to human health and the environment.

The global emission of non-methane VOCs (NMVOC) for the year 1990 is 153,244 ktones while in 1995 the amount increased to 159,634 ktones. Table 1.1 shows the national emission of VOCs for several countries in the year 1990 and 1995. Except for the US, all the other countries show an increasing emission of VOCs. Data was obtained from Emission Database for Global Atmospheric Research (EDGAR 3.2).

In this research the VOCs concerned are benzene, toluene, *m*-xylene, acetone, and tetrachloroethylene (TeCE). As these substances poses very serious health affects, the Environmental Protection Agency (EPA) of most countries considers all of these compounds priority pollutants. The concentration of single VOCs was reviewed to be generally below 15 ppb with most below 1.5 ppb (Wolkoff, 2001). However, in a given environment, the concentration of individual VOCs will be very variable and depend upon the presence or absence of potential emission source.

Table 1.1: National VOCs Emission in ktonnes (1995)

Country	1990	1995
Australia	2,377.01	2,390.73
Japan	5,435.64	5,851.56
Malaysia	1,636.93	1,938.23
Singapore	124.66	156.11
Thailand	898.9	1195.96
United Kingdom	3,360.80	3,567.10
United States	19,626.79	19,497.00

Benzene, toluene and xylene are monocyclic aromatic hydrocarbons associated with motor vehicle emissions arise predominantly from the evaporation and combustion of petroleum products. Exhaust emission constitute 80-90 % of the total emission of benzene, the highest level of exposure (Pang, 1996).

Benzene is a well-established human carcinogen and laboratory studies have shown that it exerts its effect by damaging the genetic materials of the cells. The most frequently reported health effect of benzene is bone marrow depression leading to *anaemia* (reduced red blood cells), *leucopenia* (reduced white cells) and *thrombocytopenia* (reduced blood plateles) (Wadge, 1997). The impact of benzene on human health and environment make it a worldwide concern as it is used widely in many industries. There is no specific air quality goal for benzene, however it is widely accepted that exposed to benzene should be minimized.

Toluene occurs naturally in crude oil and in *tolu* tree. Toluene is used in aviation gasoline, solvent for paints, fingernail polish, lacquer, adhesive and in some printing and leather tanning processes. Although the primary sources of toluene emissions are crude petroleum and natural gas extraction, petroleum refining and household furniture manufacturing facilities, it is also emitted from tobacco smoke. Toluene affects the nervous system and high levels of toluene may affect the kidneys. The U.S EPA has established a reference concentration of 162 ppb for toluene based on neurological effects in humans and has set a limit of 3×10^{-4} ppm in drinking water (ATSDR, 2000). The inhalation of this concentration or less, over a lifetime, would not likely result in the occurrence of chronic non-cancer effects.

Xylene occurs naturally in petroleum and coal tar and is formed during forest fires. Chemical industries produce xylene from petroleum. It is used as solvent and in the printing, rubber and leather industries. It is also used as a cleaning agent, a thinner for paint, and in paint and varnishes. Xylene affects the brain, however, human and animal studies have not shown xylene to be carcinogenic, but these studies are not conclusive. The U.S EPA has set a limit of 10 ppm of xylene in drinking water and an exposure limit of 100 ppm in the workplace air. An exposure of 900 ppm of xylene can cause permanent health problems or death (ATSDR, 1995).

Acetone is a manufactured chemical that is also found naturally in the environment. Acetone is used to make plastic, fibers, drugs and other chemicals. It is widely used in industry as solvent for numerous organic substances and is a component of most paint and varnish removers. Although acetone is not carcinogen, exposure to it can cause health effects such as eye, nose and throat irritation. High exposures may damage the liver and kidneys. Skin contact can result in irritation and damage to the skin. A permissible exposure limits for acetone is 250 ppm in the workplace (ATSDR, 1994).

Tetrachloroethyle (TeCE), also known as perchloroethylene (PCE), is a manufactured chlorinated hydrocarbon compound, mainly used as degreaser for metal parts and as a solvent in dry cleaning operations. TeCE may be a carcinogen in humans and may damage the developing fetus. It can also damage the liver and kidneys enough to cause death. The U.S EPA maximum contaminant level for the amount of TeCE that can be in drinking water is 0.005 milligrams TeCE per liter of water. It is recommended that TeCE should be handled as a potential carcinogen and exposure of TeCE at the working place should be minimized (ATSDR, 1997).

Although public concern over the health effects of VOCs is directed to outdoor pollution, the health impacts of indoor air pollution should not be neglected. Studies showed that the concentration of indoor VOCs often exceed outdoor levels by up to 5 times (Jones, 1999). Indoors air pollutants emanate from a range of sources such as fabric of buildings, paints, varnishes, aerosol sprays, cleaners, disinfectants, automotive products, dry-cleaned clothing and tobacco smoke.

VOCs have drawn considerable attention in the last decade as the health effects of these compounds are better understood. Many countries have since put stringent regulations concerning the use and emission of VOCs. Currently there is a great deal of interest in developing processes that can destroy these compounds. Since a large number of the VOCs are oxidizable, chemical oxidation process can be looked upon as a viable method.

1.2 Heterogeneous Photocatalysis

Heterogeneous photocatalysis is an emerging technique valuable for water and air purification and remediation. This method has gained significant impetus over the years as it offer the advantage of destroying a wide range of water and air pollutants. Conventional techniques such as activated carbon or air stripping are becoming unacceptable because they do not destroy the pollutants but only transfer the contaminants from one phase to another. The absolute toxicity of the pollutants, however, is not diminished.

Heterogeneous photocatalysis technique for air purification and wastewater treatment formed part of a group of processes known as *Advanced Oxidation Technologies* (AOTs). AOTs use a highly active redox reagent to bring about the complete mineralization of all atoms present in an organic pollutant (Ollis, 1988). Included among these AOTs is photocatalysis using semiconductors such as titanium dioxide. Ultraviolet light radiation on such catalysts sets in train a sequence of events that can lead to oxidation of organic (or inorganic) compounds present in water or air that is in contact with the catalyst.

In heterogeneous photocatalysis, activation of the semiconductor photocatalyst is achieved through the absorption of a photon with energy equal or higher then the catalyst band gap energy. This results in the promotion of an electron, e^- from the valence band to the conduction band, with the concomitant generation of a hole, h^+ in the valence band. This electron-hole separation, characterized by a finite lifetime, allows different chemical pathways to occur as outlined in Figure 1.1.

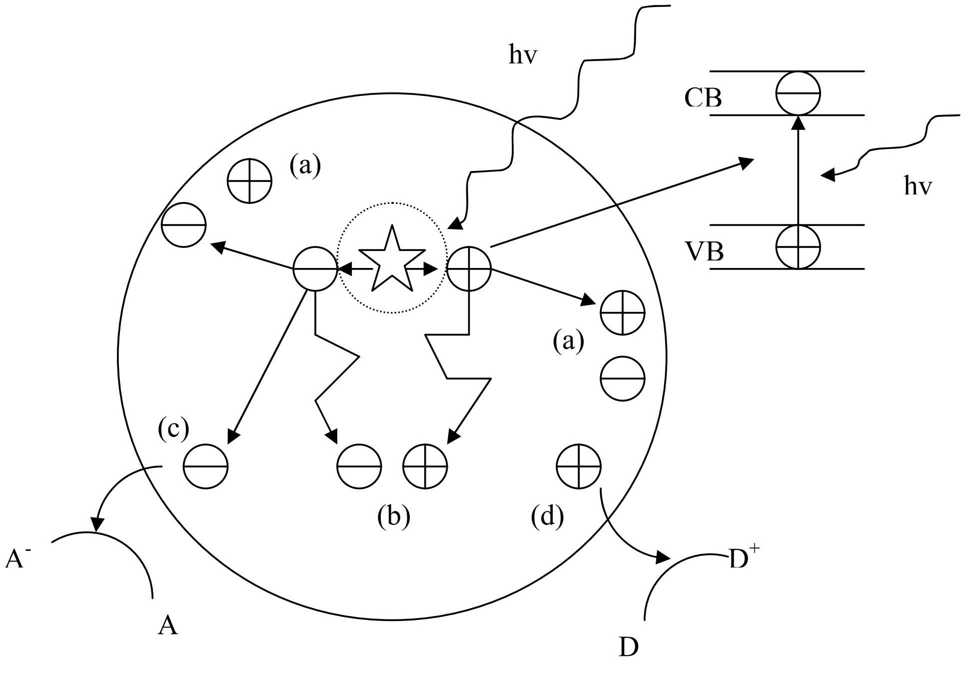

Figure 1.1: Illustration of the major processes occurring on a semiconductor particle following electronic excitation (Hoffman, 1995). (a) and (b) recombination of $e^- h^+$, (c) reduction of e^- by an electron acceptor, (d) oxidation of h^+ by electron donor

This highly reactive e^- - h^+ pairs can recombine and release heat (charge recombination) either on the surface of the semiconductor (Pathway a) or in the bulk volume (Pathway b) or migrate to the solid surface and undergo electron-transfer processes with adsorbates. The photogenerated electrons can reduced an electron acceptor A (Pathway c) and the photogenerated holes can oxidized an electron donor (Pathway d). For a semiconductor photocatalyst to be efficient, the different interfacial electron processes involving e^- and h^+ must compete effectively with the major deactivation processes involving e^- - h^+ recombination.

Once excitation occurs across the band gap there is a sufficient lifetime, in the nanosecond regime (Rothenberger, 1985) for the created electron-hole pair to undergo charge transfer to adsorbed species on the semiconductor surface from solution or gas phase contact. If the scavenger or surface defects are present to trap the electron or holes, e^- - h^+ recombination can be prevented and the subsequent oxidation and reduction processes caused by electrons and holes may be enhanced (Park, 1999). Oxygen and surface-bound hydroxyl species are believed to be the most important electron acceptor and electron donor species in photocatalytic oxidation processes, respectively.

1.3 Titanium Dioxide

In 1972, Fujishima and Honda (Fujishima, 1972) discovered the photocatalytic splitting of water on TiO_2 electrodes. This was the starting point of a new era in heterogeneous photocatalysis. Since then heterogeneous photocatalytic oxidation, using TiO_2 has been studied extensively in areas such as photovoltaic conversion and energy storage but more attention has been given in the remediation of water and air. Heterogeneous photocatalytic using TiO_2 has several attractions. TiO_2 is a relatively inexpensive compound as it is one of the most abundant minerals in the earth crust. It is chemically stable, resistant to acids and easy to handle, making it environmentally safe. TiO_2 shows efficient destruction of toxic contaminants and reacts with organic pollutant at ambient temperature and pressure, using oxygen as the oxidant, producing CO_2 and H_2O or HCl, in the case of chlorinated organic compound.

Titanium dioxide occurs in two different crystal forms known as rutile and anatase. Both crystal forms exhibit photocatalytic activity under near-UV irradiation. However, anatase is more photoactive than rutile and is therefore more widely used. For anatase, the band gap energy of 3.2 eV corresponds to UV light (388 nm) while the band gap energy of rutile (3.0 eV) corresponds to violet light (413 nm). The band gap energy indicates the minimum energy of light necessary to produce transition of electrons from valence band (VB) to the conduction band (CB). The level of CB for anatase is 0.2 eV higher than rutile as depicted in Figure 1.2 (Fujishima, 1999).

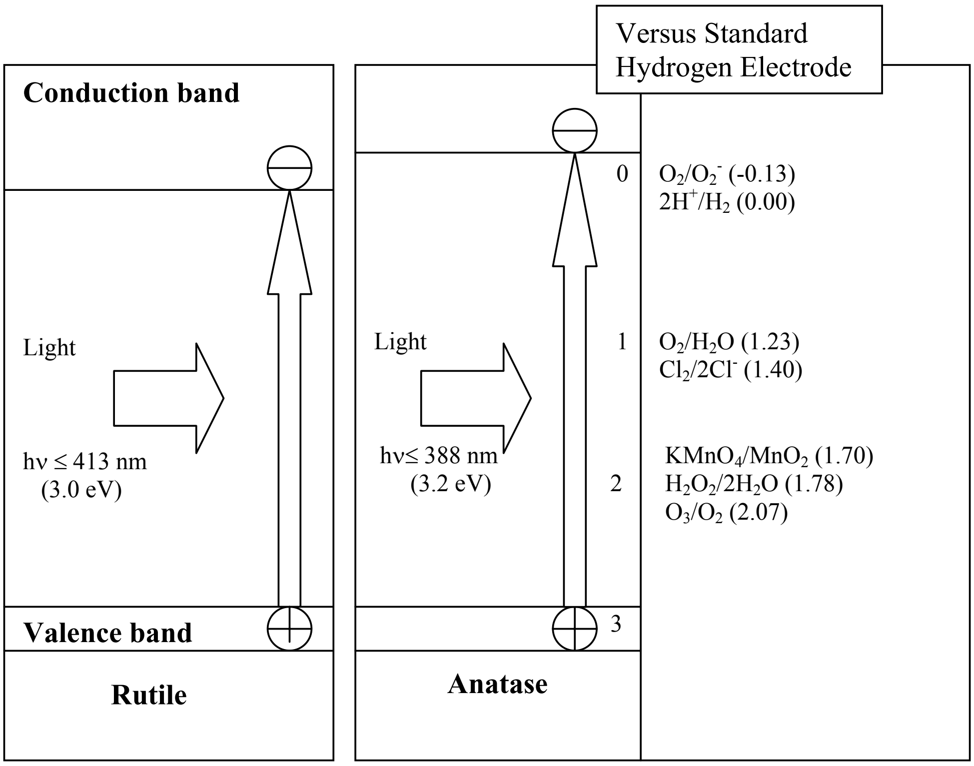

Figure 1.2: Energy diagram for TiO_2 and relevant redox potentials

The VB energies for anatase and rutile are both similar, which is very low in the energy diagram, meaning that, for both materials, the VB holes have high oxidizing power. The CB energy for rutile is close to the potential required to electrolytically reduce water to hydrogen gas, but that of anatase is higher in the energy diagram, meaning that it has higher reducing power. This means that it can drive the very important reaction involving the electrolytic reduction of molecular oxygen (O_2) to superoxide (O_2^-), which is as important as the holes and hydroxyl radicals in breaking down organic compounds.

1.3.1 Band Gap Transition

Unlike metals, which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of an electron and hole produced by photoactivation in the solid. The void region, which extends from the top of the filled valence band to the bottom of the vacant conduction band is called the band gap. The band gap is the most important optical characteristic of a semiconductor.

When light of sufficient energy is incident on a semiconductor, photons are absorbed and electronic excitations are created. Electrons at the ground state will be excited to a higher energy level. Eventually, these excitations relax and the electrons return to the ground state. Different processes participate in this relaxation, which can be categorized as either radiative process or non-radiative process (such as phonon emission, capture by deep centers or Auger effect). If radiative relaxation occurs, the emitted light is called photoluminescence (PL). The radiated recombination of excited individuals or coupled charge carriers that caused luminescence may be:(i) free electrons or holes occupying the energy levels in the conduction and valence bands respectively, in fact PL can be considered as the radiative recombination of conduction band electron with valence band hole in semiconductor (ii) electrons or holes bound to ionized impurities or dopants, and (iii) excitons (electron-hole pairs coupled by Coulomb interaction) which may move throughout the crystal lattice of the semiconductor (free excitons) or become localized by interaction with an active point defect of the lattice or on interfaces occurring in the semiconductor (bound excitons).

There are two kinds of transition that can occur in the band gap when a semiconductor absorbs photon as depicted in Figure 1.3.

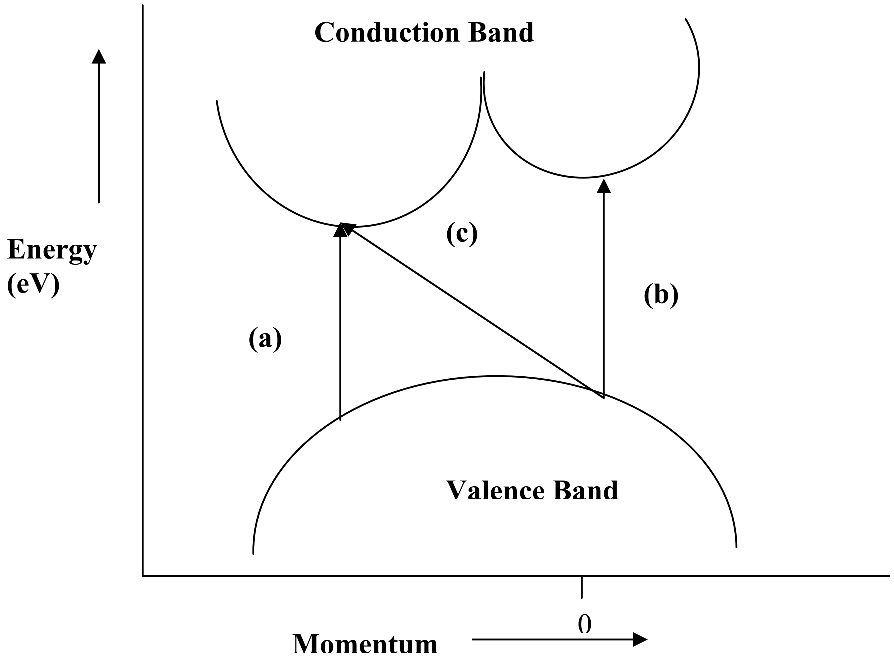

Figure 1.3: Electronic transitions in a semiconductor bands. (a), (b) direct transition and (c) indirect transition (Serpone, 1989)

When the lowest energy excitation of an electron from the valence band to the conduction band involves no change in momentum (Figure 1.3), the semiconductor is said to have a *direct band gap*. However, in an *indirect-band-gap* material, the momentum at the valence band maximum is different from that at the conduction band minimum (Figure 1.3). TiO_2 can exhibit both indirect and direct transition but the former transition was much accepted.

1.3.2 Doping

It can be seen that the essence of a photocatalytic mechanism is the production of photogenerated electron and hole. The ease of production and separation of these reactive species will consequently increase the photocatalytic activity of TiO_2. Therefore the smaller the band gap, the higher the production of the electron and hole. It can be seen from Section 1.3.1 that the transition energy of an electron from the VB to CB can change with the existence of impurities or dopant in the semiconductor. Doping implies incorporation of a foreign cation into the catalyst matrix of the parent metal oxide (Karakitsou, 1993). From a chemical point of view, TiO_2 doping is equivalent to the introduction of defect sites into the semiconductor lattice (Fox, 1993). A wide range of metal ions in particular transition metal ions, have been used as dopants in the effort to increase the photocatalytic reactivity of TiO_2.

In the bulk of crystalline material, translational symmetry leads to the formation of electronic energy bands. Dopants break the periodicity of the lattice and perturbed the band structure locally. The perturbation usually can be characterized by a discrete energy level that lies within the band gap. Therefore new energy levels in the band gap are created when dopants are introduced inside the semiconductor. If the new level lies between the VB and CB, the photocatalytic activity of the semiconductor is enhanced, as lower transition energy is required (Figure 1.4).

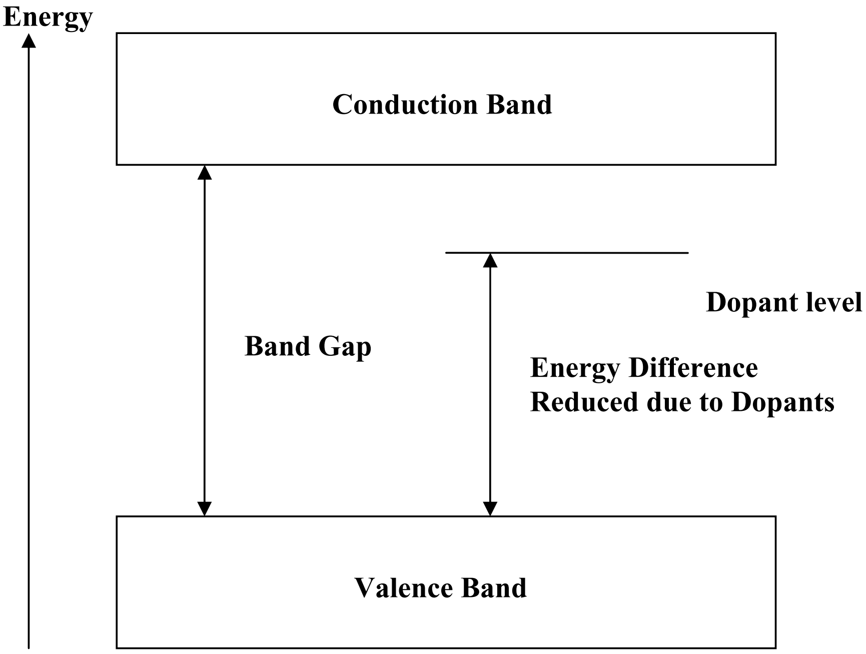

Figure 1.4: Energy Difference Reduced due to Dopant

Besides lowering the transition energy of electron, metal ion dopants influence the photoreactivity of TiO_2 by acting as electron (or hole) traps and by altering the e^-/h^+ pair recombination rate through the following process.

$M^{n+} + e_{cb}^- \rightarrow M^{(n-1)+}$ electron trap

$M^{n+} + h_{vb}^+ \rightarrow M^{(n+1)+}$ hole trap

Where the energy level for $M^{n+}/M^{(n-1)+}$ lies below the conduction band edge (E_{cb}) and the energy level for $M^{n+}/M^{(n+1)+}$ above the valence band edge (E_{vb}). Available energy levels of metal ion impurities in TiO_2 are shown in Figure 1.5 (Litter, 1996).

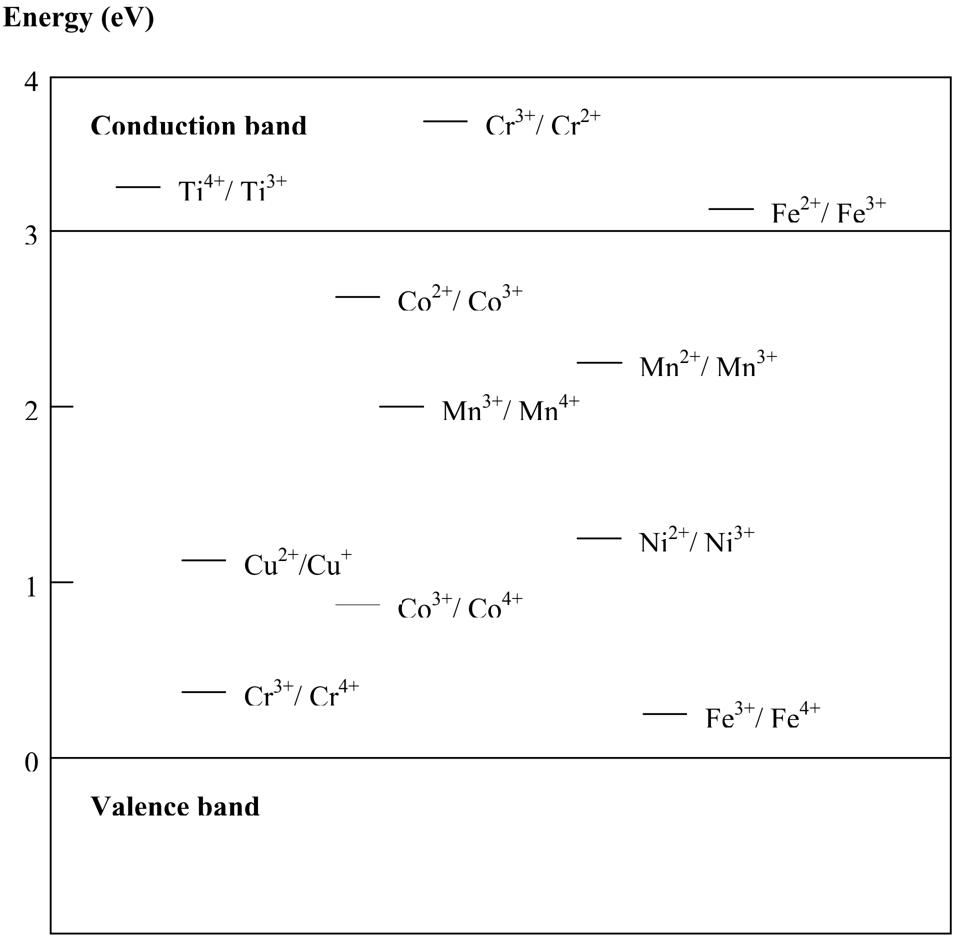

Figure 1.5: Energy levels of dopant ions (Litter, 1996). Energy level of Zn^{2+} was not available.

The introduction of such energy levels in the band gap will induce a red shift (lower energy) in the band gap transition and the visible light absorption through a charge transfer between a dopant and CB (or VB) or a d-d transition in the crystal field (Choi, 1994). The incorporation of metal ions into TiO_2 crystal lattice, therefore, can significantly extend the absorption by the photocatalysts into the visible region.

It should be stressed that dopants should act as both electron traps and hole traps to be photoactive (Choi, 1994). Trapping either electron or hole alone is ineffective because the immobilized charge species quickly recombines with its mobile counterparts. The photoactivity of doped TiO_2 photocatalyst, however, substantially depends on the dopant ion nature and concentration, besides the preparation method and the thermal and reductive treatment (Malati, 1984).

1.3.3 Reaction Pathway

Titanium dioxide photocatalytic technology has been widely studied as a potential method for the purification of water and air contaminated with various pollutants. It is well established that hydroxyl radical implicated as the reactive species in the photocatalytic oxidation of many organic compounds in liquid-solid systems as well as in gaseous phase systems (Phillips, 1992) are formed through the capture of holes, by surface water molecules and/or hydroxyl ions or surface titanol groups (Hoffman, 1995). These reactive •OH species can readily oxidize organic substrate absorbed on the catalyst surface.

Hydroxyls are formed as a result of dissociative chemisorption of H_2O onto the Ti^{4+} sites and water can be physiorbed on the surface hydroxyl groups via hydrogen bonding (Raupp, 1985). Oxidative electron transfer occurs exclusively through these surface bound hydroxyl radical or equivalent trapped hole species. In a gas solid system, however, since water molecules are not the predominant species in contact with the catalyst in the gas phase, direct oxidation may occur via the valence band hole as the organic substrate can themselves act as adsorbed traps for the photogenerated holes (Alberici, 1997; Shang, 2002). The role of hydroxyl groups is now established as traps for photogenerated valence band holes thereby retarding the electron-hole recombination. The reaction of hole in the heterogeneous photocatalytic can be express by the following set of equations (Hoffmann, 1995)

$$TiO_2 + h\nu \rightarrow TiO_2\,(h^+_{VB} + e^-_{CB}) \tag{1.1}$$

$$TiO_2\,(h^+_{VB}) + H_2O_{ads} \rightarrow TiO_2 + \bullet OH_{ads} + H^+ \tag{1.2}$$

$$TiO_2\,(h^+_{VB}) + OH^-_{(surface)} \rightarrow TiO_2 + \bullet OH_{ads} \tag{1.3}$$

$$TiO_2\,(h^+_{VB}) + D_{ads} \rightarrow TiO_2 + D^+_{ads} \tag{1.4}$$

$$\bullet OH + D_{ads} \rightarrow D_{oxid} + H_2O \tag{1.5}$$

D_{ads} is an electron donor species generally the organic compounds adsorbed on the catalyst and oxidized to D^+_{ads} when reacted with the h^+ in TiO_2. In the presence of oxygen, O_2, superoxides (O_2) ions are also generated. This species subsequently react with protons and adsorbed H_2O from the hydrated surface produces hydroperoxide radicals, HO_2, which is another source of OH radicals (Herrmann, 1979; Augugliaro, 1999).

$$Ti^{4+} + e^- \rightarrow Ti^{3+} \tag{1.6}$$

$$\text{and}\quad Ti^{3+}_{(surface)} + O_{2\,(ads)} \rightarrow Ti^{4+} + O^-_{2\,(ads)} \tag{1.7}$$

$$\text{Or}\quad O_{2\,(ads)} + e^- \rightarrow O^-_{2\,(ads)} \tag{1.8}$$

$$O^-_{2\,(ads)} + H^+ \rightarrow HO_2\bullet \tag{1.9}$$

$$\bullet OH + O^-_{2\,(ads)} \rightarrow HO_2\bullet + O^-_{(ads)} \tag{1.10}$$

$$2HO_2\bullet \rightarrow O_2 + H_2O_{2\,(ads)} \tag{1.11}$$

Sopyan *et al*. (Sopyan, 1996) have confirmed the production of H_2O_2 by the reduction of O_2 using a microelectrode technique. The hydrogen peroxide production is subsequently followed by hydroxyl radical-forming reaction such as equation (1.12) and (1.13).

$$H_2O_{2\,(ads)} + O^-_{2\,(ads)} \rightarrow OH^- + \bullet OH + O_2 \tag{1.12}$$

$$Ti^{3+}_{(surface)} + H_2O_{2\,(ads)} \rightarrow Ti^{4+} + \bullet OH + OH^- \tag{1.13}$$

Or via direct photolysis (Sopyan, 1996)

$$H_2O_2 \quad + \quad h\nu \quad \rightarrow \quad 2\,\bullet OH \qquad (1.14)$$

These OH radicals, being deficient of one electron, are electrophiles capable of migrating and carrying out oxidative destruction of organic molecules absorbed on the catalyst surface (Linsebigler, 1995). In fact, the destruction of organic molecules via the mechanism of radical attack is the hallmark of advanced oxidation process.

1.3.4 Kinetic Study

Reaction kinetics gives information about the reaction rates and the mechanisms by which the reactants are converted to the products. To photocatalytic oxidation, the rate law was used to predict reaction rate. Theoretically, the reaction rate can be simply expressed as the decreasing rate of any of the reactants or the increasing rate of any of the products against time. A common way to express the reaction rate is to use the rate law: rate = $-d[A]/dt = k[A]^n$, where k is the rate constant, n is the order of the reaction and [A] is the concentration of reactant A. The reaction rate of photocatalytic oxidation represents the efficiency of photooxidation reaction and it can be influenced by such factors as humidity, light intensity, contaminant concentration and oxygen concentration.

A necessary step of a photocatalytic reaction is that the reactant molecules are adsorbed on the catalyst surface. The fact that only adsorbed species can be oxidized makes the adsorption process very important in the photocatalytic oxidation process. The Langmuir-Hinshelwood (L-H) mechanism for surface catalysis is widely used to describe the heterogeneous gas-solid reaction. These mechanisms consist of four different steps *i.e.* adsorption from the gas-phase, desorption to the gas-phase, dissociation of molecules at the surface and reactions between adsorbed molecules. With this reaction mechanism, the reacting components at the active centers of the catalyst must be adsorbed. This L-H model has been shown to provide a quantitative kinetics treatment of many solid gas reactions (Jacoby, 1995; Nimlos, 1996; Alberici, 1997; Bouzaza, 2002, Shang, 2002; Zhao, 2003). It includes the assumption that the Langmuir adsorption isotherm is valid for the surface reaction.

In general, the kinetics of heterogeneous catalysis would follow the L-H model, in which the reaction rate (*r*) of a unimolecular surface reaction varies proportionally with the surface coverage (θ) as:

$$r = k\theta = \frac{kKC}{1+KC} \tag{1.15}$$

$$\frac{1}{r} = \left(\frac{1}{kKC} + \frac{1}{k}\right) \tag{1.16}$$

where, *k* and *K* are the reaction rate constant and the adsorption equilibrium constant, and *C* is the concentration of VOCs (Ollis, 1991). A linear plot of the reciprocal value of the initial rate ($1/r$) against the reciprocal values of the organic compound initial concentration ($1/C_o$) gives *k* as the L-H rate constant and *K* as the Langmuir adsorption constant of the VOCs in the photocatalytic degradation reaction. Although in the presence of water vapour, OH groups are present on the TiO_2 surface and their contribution to photooxidation cannot be discarded, the preliminary adsorption of organic compound is very important pre-requisite for highly efficient detoxification.

Pseudo-first-order reaction can be resulted from the L-H rate equation only when the term KC_0 is much less than 1 ($KC \ll 1$). L-H equation is often applied to evaluate the L-H rate constant *k* and the adsorption constant *K*, but it is only valid at the initial stage. During the photocatalytic process, intermediates are formed and their *KC* terms must be included in the L-H rate equation even when their adsorption on the TiO_2 surface may be rather weak. For simplicity, however, it is better to employ the initial VOCs rate for the application of the equation. This can be done by an assumption that at initial time interval, the intermediate concentration can be considered to be negligible. Definitely, such an initial time interval should be as short as possible. In practice, however, a considerable error in the analysis would be made easily for such a small conversion of the substrate. So for this study the initial rate will be calculated for the first 15 minutes of the reaction time.

1.3.5 TiO_2 Thin Film

Most studies in heterogeneous photocatalytic oxidation of organic contaminants either in air or aqueous solution have been performed with powder TiO_2 particularly in anatase form (Pruden, 1983; Hisanaga, 1990; Peral, 1992; Alberici, 1997). However, several practical problems with using powders in photochemical processing are apparent. In aqueous phase reaction, the separation of the catalyst from the suspension after the reaction is difficult. The suspended particles also tend to aggregate, especially when they are present at high concentrations. Particulate suspensions are also not easily applicable to continuous flow systems.

In a packed bed photoreactor used for gas phase photooxidation, the distribution of the catalyst in the reactor is not uniform due to the non-uniform sizes and shapes of the photocatalysts particles. As a result most of the catalyst is probably not illuminated by the UV light, especially the portion in the interior of the porous particles (Fu, 1995). This so-called “shadowing effect” has also been observed in previous studies (Wei, 1991).

In order to alleviate these problems, the engineering properties of TiO_2 must be improved and several approaches have been taken by researchers in this field. One of the most widely used techniques is to immobilize the TiO_2 as thin film on various supports including glass, stainless steel, quartz, silica gel and glass beads.

The idea of immobilizing TiO_2 in the form of thin film was first recognized by Fujishima and Honda (Fujishima, 1972). They found that the thin film photocatalysts have a lower surface area than powdered form, resulting in a lower photocatalytic activity. However, several researches collected data later showed that thin film TiO_2 had a porous structure and exhibited high photoactivity towards organic degradation. Since then TiO_2 thin film emerged as a plausible photocatalyst in environmental applications. TiO_2 immobilized on various supports can be separated from the effluent much easier than its powder form (Anderson, 1995) and it can eliminate the problem of shadowing effect.

TiO_2 thin films have been prepared by variety of deposition techniques such as chemical vapor deposition (Babelon, 1998), reactive sputtering (Mardare, 2002; Liu, 2002), atomic layer deposition (Aarik, 2000), filtered arc deposition (Bendavid, 2000), pulse laser deposition (Sumita, 2002) and spray pyrolysis (Abou-Helal, 2002; Castaneda, 2002). However, the sol-gel method is the most commonly used method for the preparation of thin film (Sopyan, 1996; Noguchi, 1998; Xu, 1999a; Zorn, 2000; Blount, 2001).

Thin films formed using sol-gel technique (Brinker, 1991a) represent the oldest commercial application of sol-gel technology. In the sol-gel process a solution containing titanium-alkoxide is first prepared. The solution is then hydrolyzed to produce crystalline TiO_2 colloids. The sol-gel derived thin films are generally prepared by the dip- or spin coating of solutions of precursor molecules or sol solutions on substrates, followed by drying and heating process. This procedure can be repeated to increase the number of TiO_2 layer and its thickness. The quality of the resulting thin film is largely dependent not only on the properties of the coating solution (density, viscosity) but also on the pulling or spinning speed (Brinker, 1991). However, thin film by dipping used little raw materials and may be processed quickly without cracking, overcoming most of the disadvantages of sol-gel processing. In addition large substrate may be accommodated and it is possible to uniformly coat both sides of planar and axially symmetric substrates. Research on the use of TiO_2 thin film as a photocatalyst in air treatment however is very few but the modest data collected is sufficient enough to show that TiO_2 thin film has high photocatalytic efficiency in the photocatalytic oxidation of various VOCs.

1.3.6 Limitations of TiO_2

Most of heterogeneous photocatalysis report of the last decade, have dealt with aqueous solutions, exploring water decontamination and purification by the photoassisted oxidative destruction of hazardous solutes (Chemseddine, 1990; Hidaka, 1992; Herrmann, 1999; Fabiyi, 2000; Tanaka, 2000; Axelsson, 2001). Studies involving gas phase heterogeneous photocatalysts are far fewer, but the modest existing literature has been demonstrated that near-UV illumination in concert with anatase titanium dioxide (TiO_2) powdered photocatalyst and molecular oxygen can carry out the complete oxidation of a wide range of organic compounds.

However, most of the researches on gas phase photocatalysis have focused only on low concentration VOCs. Peral (1997) even suggested that heterogeneous photocatalysis is a promising new technology for the removal of dilute levels of organic contaminants in air rather than highly concentrated volatile organics. As the concentration of VOCs is higher in an industrialized area, a new improved TiO_2 catalyst that can destroy both low and high concentration of VOCs is therefore needed.

Heterogeneous catalytic oxidation technology for gas phase pollution control has well been established in automotive exhaust and catalytic incineration. However, nearly all heterogeneous oxidations catalyst functions at elevated temperatures, whereas nearly all inhabited atmospheres of concern to humans exist at or near 20-25°C. A need, therefore exist for an air purification catalyst which can not only function at ambient conditions of temperature and pressure, but can also use the mildest and most prevalent oxidant, molecular oxygen (O_2) and is active against the broadest possible range of contaminant structures (Hager, 2000).

Photocatalysis oxidation of VOCs using TiO_2 has shown great potential in the field of air treatment. It gives a rapid and efficient destruction of a wide spectrum of low-level air pollutants (Hoffman, 1995). However, the light usable in the photocatalytic reaction of TiO_2 is limited to light with wavelength lower than 400 nm (Fujishima, 1999). Materials that can use visible light would be more desirable in terms of the effective utilization of ordinary light. For that reason, the current research on TiO_2 has been focused on catalyst modification, in the effort to search for a semiconductor that supports photocatalytic reactions with high efficiency and with the use of visible light.

There is also a growing interest in the use of thin transparent films of TiO_2 as a sensitizer for the photodestruction of gaseous organic species, thereby generating a photodeodorizing surface, but also thin film that can generate a self cleaning surface.

The later film could find application in self-cleaning windows and automotive windshields. Such TiO_2 films need to be clear (*i.e.* they must not scatter visible light), adherent (with an abrasion resistance which is sufficient to withstand cleaning or impact by dust particles) and photoactive. The photoactivity must be such that it is greater than the rate of deposition, otherwise it will become fouled with UV-adsorbing non-volatile partial oxidation products.

1.4 Research Objectives

The aim of this research is to develop a photocatalyst with high photoactivity, which is stable and capable of degrading and mineralizing a wide class of recalcitrant VOCs using ultra violet light. The specific objectives of this research are:

- To develop transparent thin film TiO_2 photocatalyst with excellent photocatalytic activity.
- To improve the photoactivity of the thin film by doping with metal ions.
- To degrade noxious gases to non-toxic gases using the prepared TiO_2 and modified TiO_2 thin film.
- To study the chemical, physical and optical properties of the photocatalysts in terms of their chemical content, morphology and band-gap energy.
- To study the mineralization of VOCs during the photooxidation process using undoped and doped TiO_2.

1.5 Scope of Study

This research is focused in developing a photocatalyst with high photocatalytic activities to degrade only gas phase hydrocarbons. The scopes of this study are listed below.

- The introduction of dopants (transition metal ions) into TiO_2 catalyst to enhance the photocatalytic activity of TiO_2.
- The photodegradation testing of VOCs gases are conducted at laboratory scale using home built photocatalysis reactor.
- The characterization studies such as film surface morphology, elemental analysis and band-gap values will be carried out.
- The volatile organic compounds under study are benzene, acetone, toluene, *m*-xylene and tetrachloroethylene.
- The photocatalytic studies will be carried out under ambient temperature and pressure.

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