

CHAPTER III

THEORY

In this chapter, the details are divided into two sections. The former part relates to physical and chemical properties of titanium (IV) oxide including preparation procedure and its advantages. The later section describes the photocatalytic process and the main factors involved in photocatalytic process.

3.1 Titanium (IV) oxide

3.1.1 Physical and Chemical properties

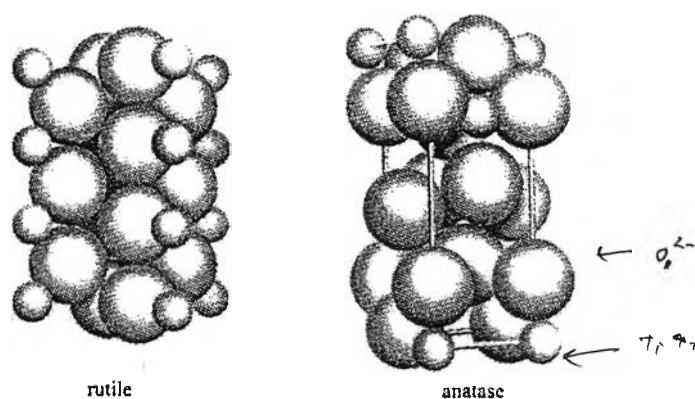
Titanium (IV) oxide occurs naturally in three crystalline forms: anatase, brookite, and rutile. These crystals are substantially pure titanium (IV) oxide but usually contain small amounts of impurities, e.g., iron, chromium, or vanadium, which are darken them. A summary of the crystallographic properties of the three varieties is given in Table 3.1

Although anatase and rutile are both tetragonal, they are not isomorphous. Anatase occurs usually in near-regular octahedra, and rutile forms slender prismatic crystals, which are frequently twinned. Rutile is the thermally stable form and is one of the two most important ores of titanium.

The three allotropic forms of titanium (IV) oxide have been prepared artificially but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystals. The transformation from anatase to rutile is accompanied by the evolution of ca. 12.6 kJ mol^{-1} ($3.01 \text{ kcal mol}^{-1}$), but the rate of transformation is greatly affected by temperature and by the presence of other substances which may either catalyze or inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is ca. 700°C , but this is not a transition temperature. The change is not reversible; ΔG for the change from anatase to rutile is always negative.

Table 3.1 Crystallographic properties of anatase, brookite, and rutile

Property	Anatase	Brookite	Rutile
crystal structure	Tetragonal	Orthorhombic	Tetragonal
optical	uniaxial, negative	Biaxial, positive	uniaxial, positive
density, g ml ⁻¹	3.9	4.0	4.2
hardness, Mohs scale	5.5 – 6.0	5.5 – 6.0	7.0 – 7.5
Dimension, nm			
A	0.3758	0.9166	0.4584
B	-	0.5436	-
C	0.9514	0.5135	2.953

**Figure 3.1** Crystal structure of rutile and anatase type TiO₂ [Fujishima et al. (1999)]

Both of rutile and anatase types have a structure belonging to the tetragonal crystal system and they are showed in figure 3.1. The two tetragonal crystal types are more common because they are easy make.

Brookite has been produced by heating amorphous titanium (IV) oxide, prepared from an alkyl titanates of sodium titanate with sodium or potassium hydroxide in an autoclave at 200 to 600°C for several days. The important commercial forms of titanium (IV) oxide are anatase and rutile, and these can readily be distinguished by X-ray diffraction spectrometry.

Titanium (IV) oxide is thermally stable (mp 1855°C) and very resistant to chemical attack. When it is heated strongly under vacuum, there is a slight loss of oxygen corresponding to a change in composition to $\text{TiO}_{1.97}$. The product is dark blue but reverts to the original white color when it is heated in air.

3.1.2 Preparation procedure

Large surface area titanium (IV) oxide powders have been prepared by several methods. The physical and chemical properties of titanium (IV) oxides are quite different by the process of preparation.

3.1.2.1 Hydrothermal method

Hydrothermal methods utilize water under pressure at temperatures above its normal boiling point as a means of speeding up the reactions between solids. The water performs two roles. The water, as liquid or vapor, serves as the pressure transmitting medium. In the addition, some or all of the reactance are partially soluble in the water under pressure and this enables reaction to take place in, or with the aid of, liquid and/or vapor phases. Under these conditions, reactions may occur that, in the absence of water, would occur only at much high temperatures. The method is therefore particularly suited for the synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arranging for a suitable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

Titanium (IV) oxide particles were preparation by hydrothermal method form titanium tetra ethoxide, $(\text{Ti}(\text{OC}_2\text{H}_5)_4)$. The results show that spherical amorphous monodispersed titanium (IV) oxide particles were synthesized by hydrolysis of titanium tetra ethoxide in dilute ethanol solution and were hydrothermally treated using an autoclave. The amorphous monodispersed titanium (IV) oxide particles were crystallized and many-sized particles of anatase single

crystal produced in the particle by the hydrothermal treatment. The internal microstructure of the hydrothermally treated monodispersed titanium (IV) oxide had specific surface area $113 \text{ m}^2 \text{ g}^{-1}$ and crystallite size which determined by XRD was 17 nm.

3.1.2.2 Glycothermal method

Glycothermal method has been developed for synthesis of metal oxide and binary metal oxide by using glycol solvents such as 1,4 butanediol instead of water in hydrothermal method. The use of glycol instead of water in synthetic procedure, intermediate phase occurred to be different form and have found that stabilities of the intermediate phase by this method was not strong so, this intermediate phase was easily converted to product under quite mild condition.

Titanium (IV) oxide particles were prepared by glycothermal method from reaction of titanium tetra-tert butoxide with 1,4 butanediol at 300°C under autoclave condition yield nanocrystalline anatase titanium (IV) oxide with diameter of 17 nm and surface area $\sim 90 \text{ m}^2 \text{ g}^{-1}$. These titanium (IV) oxides were thermally stable.

As described above in literature review section, similar treatment in other organic solvents such as inert organic solvent and/or alcohol solvents gave nanocrystalline titanium (IV) oxide. The physical and chemical properties of this product depended on kind of organic solvents and reaction conditions.

3.1.3 Titanium (IV) oxide usages

3.1.3.1 Pigment usages

Titanium (IV) oxide pigment. Properties: The high refractive index, lack of absorption of visible light, ability to be produced in the correct size range, and the stability and nontoxicity of titanium (IV) oxide are the reasons why it has become

the predominant white pigment in the world. Titanium (IV) oxide pigments are produced in rutile form. These names indicate that the pigments have the same crystal structure as the minerals of those names indicate but do not necessarily indicate that they have been made from those ores.

Raw materials: The raw materials in the manufacture of titanium pigments are ilmenite and rutile. Titanium (IV) oxide pigments are produced by two processes, i.e., the classical sulfate process and the chloride process. In the first, by which the bulk of the world's pigment is produced, the essential step is hydrolysis under carefully controlled conditions of an acid solution of titanyl sulfate, followed by calcination of the hydrous precipitate. In the second, the essential step is burning titanium tetrachloride in oxygen to yield titanium (IV) oxide and chlorine. These two routes make use of the two feasible methods in which titanium ores react by solution in sulfuric acid and by chlorination in the presence of a reducing agent.

3.1.3.2 Nonpigment usages

An important use for titanium (IV) oxide is in the production of components for electronic equipment. Its high resistance makes it ideal for use in the miniaturization of capacitors. These are made by pressing high purity rutile into the desired shape and then heating the pressing until the particles sinter at ca. 1400 to 1450°C. Additions of materials, e.g., clay, assist in producing the mold and reduce the firing temperature. These additions must be kept small to avoid adverse effects on the electrical properties of the product.

Many substances have been added to titanium to improve or modify its electrical characteristics. Some of these, e.g., zirconium (II) oxide, simply act as diluents but others, e.g., barium oxide, form mixed oxides or titanates, which can also be manufactured and used independently.

Synthetic gems have been produced from rutile and strontium titanate. The high refractive index of these materials results in gems of high brilliance. The

stones also provide a fine display of colors because of their high dispersion, which is superior to that of diamond. However, they are not very hard.

Mineral rutile is used as an ingredient of welding-rod coatings, for which impurities such as iron are acceptable.

Titanium (IV) oxide is used increasingly as a catalyst, either as an active agent of an inert support. The catalytic oxidation of o-xylene to phthalic anhydride using a mixture of titanium (IV) oxide and vanadium pentoxide as catalyst on an inert support is a well-established commercial process. The same agents have also been used for the reduction of nitrogen oxides in exhaust gases from internal combustion engines. Titanium (IV) oxide has also been used as an oxygen sensor to monitor automobile engine performance; the feedback from the detector controls the air-fuel ratio, giving optimum low pollution performance.

Titanium (IV) oxide impregnated with precious metals (e.g., platinum, rhodium, or ruthenium) or nickel is used in the Fischer-Tropsch synthesis for the production of hydrocarbons from carbon monoxide and hydrogen. There are many researches in the photocatalytic splitting of water to give hydrogen, which is used as a fuel.

Numerous other reactions, which as yet are only of academic interest, have been studied in which titanium (IV) oxide is used as a catalyst. These include the oxidation of hydrogen sulfide to sulfur dioxide, the dehydration of alcohols, ammonoxidation, methylation, isomerization, and alkylation.

3.2 Photocatalytic process [Fujishima et al. (1999)]

There are two main factors involved in photocatalytic process. Photocatalysis is the combination of photochemistry and catalysis, it implies that light and catalyst are the main factors, which initiate the chemical transformation, oxidation and

reduction reactions. Light is not only one, which can work effectively, but it, can work effectively when teamed up with catalyst especially titanium (IV) oxide catalyst.

The primary photocatalytic process occurring upon irradiation of a semiconductor catalyst or photocatalyst. Semiconductors such as TiO_2 , ZnO , SrTiO_3 , K_4NbO_2 , Fe_2O_3 , and SnO_2 are characterized by an electronic band structure in which the highest occupied energy band, called valence band, and the lowest empty band called conduction band, are separated by a band gap. The magnitude of the fixed energy gap between the electronically populated valence band and the largely vacant conduction band governs the extent of thermal population of the conduction band in its intrinsic state. The band gap also defines the wavelength sensitivity of the semiconductor to irradiation.

Especially titanium (IV) oxide (TiO_2), titanium (IV) oxide is one of the most basic materials in our daily life. It also has been used widely in photocatalytic process because of its radiation stability, non-toxicity and good reactivity [Alberici and Jardim (1997)]. Naturally, the type of titanium (IV) oxide used as a pigment is different from that used as a photocatalyst. Might say that titanium (IV) oxide has two aspects but one set of properties. Titanium (IV) oxide is a semiconductor and is chemically activated by light energy. Its photoactivity tends to decompose organic materials that come in contact with it.

One of the reasons for the anatase type titanium (IV) oxide is more photoactive than the rutile type and may lie in the differences in their so-called energy and structures.

The band gap energy of a semiconductor is the minimum energy of light required making the material electrically conductive or in the other words, to get the electrons excited enough to get moving. For anatase titanium (IV) oxide this energy is 3.2 electron volts (eV), which corresponds to UV light (388 nanometers), while the band gap energy for the rutile type is 3.0 eV, corresponding to violet light (413

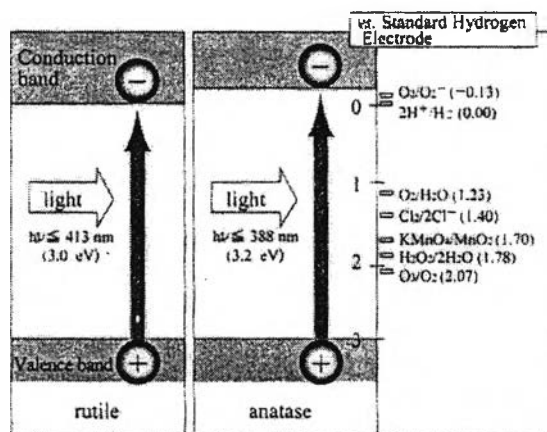


Figure 3.2 Energy diagram for TiO₂ and relevant redox potentials [Fujishima et al. (1999)].

nanometers). In more technical terminology, the band gap energy for a semiconductor indicates the minimum energy of light necessary to produce conduction band electrons, which, for example, can give rise to electrical conductivity (photoconductivity) and valence band holes, which are actually the absence of electron. These holes can react with water to produce the highly reactivity hydroxyl radical ($\cdot\text{OH}$). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic materials. The level of the conduction band for anatase turns out to be 0.2 eV higher than that for rutile (figure 3.2).

The valence band energies for anatase and rutile are both similar, which is very low in the energy diagram, meaning that, for both materials, the valence band holes (and the hydroxyl radicals) have great oxidizing power. The conduction energy for rutile is close to the potential required to electrolytically reduce water to hydrogen gas, but that for 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 ($\cdot\text{O}_2^-$). Superoxide is found that it's almost as important as the holes and hydroxyl radicals in breaking down organic compounds.

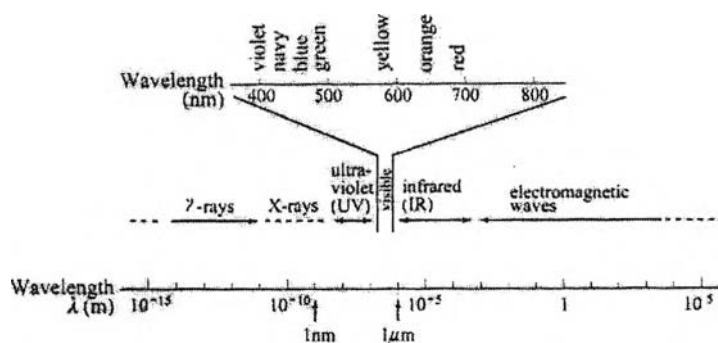


Figure 3.3 The spectrum of light [Fujishima et al. (1999)].

The second factor, light, is a form of energy characterized by waves, can be classified by wavelength, which is the distance between wave crests as indicated in figure 3.3. The light visible to eyes is only small part of total light spectrum, this range from about 400-700 nanometers. But the visible light is not usually used for the photocatalytic process because the most active and usually used catalyst for this process is titanium (IV) oxide which has band gap energy is about 3.0 eV or 400 nanometer, which falls in the near ultraviolet (figure 3.4). Photoexcitation of photocatalyst molecule involving absorption of energy equal to the energy difference between electron states using, so near UV or UV light (300-400 nanometer) is used for photocatalytic process.

Ultraviolet light, which includes wavelengths shorter than 400 nanometers. Although UV light is a part of solar light and even interior lighting, it is only limited part. Even in the outdoors, during daytime, UV light constitutes only about 1 mW cm^{-2} at the most. UV light, however, can work effectively when teamed up with titanium (IV) oxide.

When a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor particle, an electron from the valence band is promoted to the conduction band with simultaneous generation of an electronic vacancy or hole (h^+) in the valence band. Figure 3.5 shows the photocatalytic process occurring on an illuminated semiconductor particle.

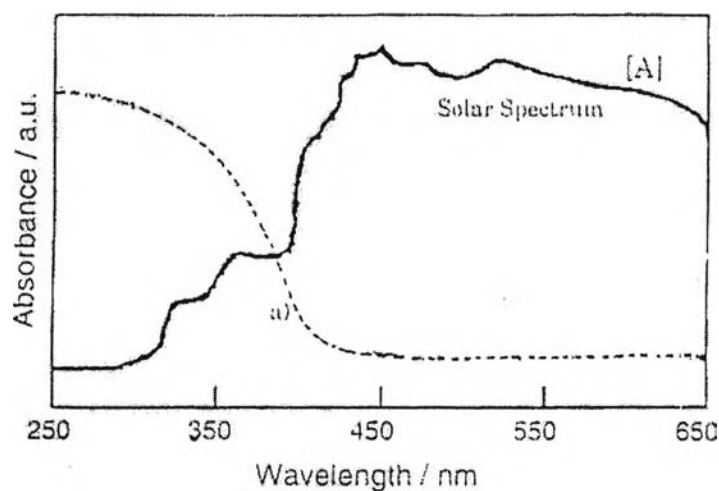


Figure 3.4 The absorption band of the TiO₂ photocatalyst to solar spectrum [Fujishima et al. (1999)].

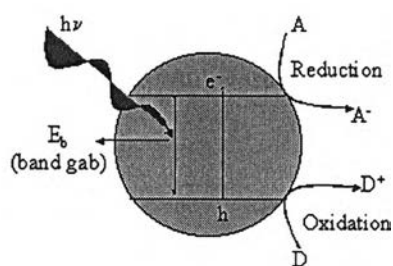
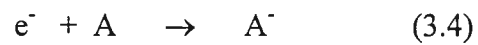
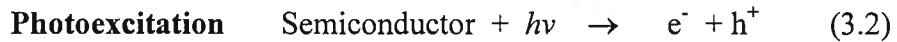
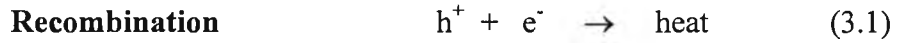


Figure 3.5 The photocatalytic process occurring on an illuminated semiconductor particle [Litter (1999)].

In most materials that are electrically conductive, i.e., metals, two types of carriers – electrons (e^-) and holes (h^+) – immediately recombine on the surface (surface recombination) or the bulk of particle (volume recombination) in a few nanoseconds and the energy dissipated as heat (equation (3.1)). On semiconductor such as titanium (IV) oxide, however, they survive for longer periods of time to allow

these carriers to be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or closed to the surface of the particle (equations (3.2)-(3.4)) [Litter (1999)].



Thereby, subsequent oxidation and reduction can be initiated.

In aqueous solution, hydroxyl radicals ($\cdot\text{OH}$) production is favored because of the abundance of hydroxyl groups and water molecules on the surface of catalyst. However, in the gas phase, organic substrates can themselves act as adsorbed traps for the photogenerated hole since in the gas phase, water molecules are not the predominant species in contact with the catalyst. Although in the presence of water vapor, OH groups are presented on the catalyst surface and their contribution to photo-oxidation cannot be discarded [Alberici and Jardim (1997)].

When adsorbed water molecules are oxidized by holes, hydroxyl radicals, which have strong oxidizing power are formed (equations (3.5), (3.6)).



The hydroxyl radicals can then react with organic components, initially producing free radicals (unstable molecules that have one unpaired electron). When molecular oxygen is present (reactions always occur in the presence of oxygen from the air in the use of the photocatalyst for environment), because it also has unpaired electrons, it likes to react with these free radicals producing organic peroxy radicals, which, in addition to containing an unpaired electron, also now contain two oxygens.

These radicals can then take part in chain reactions. In a short time, organic compounds are completely degraded, i.e., converted into carbon dioxide and water.

Meanwhile, the electrons that are produced in the electron-hole pairs are also put to work. These electrons are used to reduce (i.e., add electrons) oxygen in air. Because oxygen is easier to reduce than water, it will tend to be reduced, producing the superoxide radical anion ($\cdot\text{O}_2^-$) (equation 3.7).



The superoxide anion attaches itself to the peroxy radicals mentioned in the previous paragraph. The resulting unstable product now contains at least four oxygens and can decompose to produce a carbon dioxide molecule. On the molecular scale, superoxide acts like a supercharge, greatly increasing the oxidation process, which is in fact a form of combustion. In addition to this mechanism, another interpretation proposed recently is that the formation in air of so-called atomic oxygen ($\cdot\text{O}$), which is extremely reactive, directly acts on the carbon bonds in organic material.

3.2.1 Inhibition of electron-hole recombination by oxygen

The rates and efficiencies of photoassisted degradation of organic substrates are significantly improved in the presence of oxygen or by the addition of several inorganic oxidizing species, such as peroxydisulfate, periodate, and peroxides. The effect of molecular oxygen is primarily as an efficient conduction band electron trapping and suppressing electron-hole recombination.

Electron trapping similarly suppresses electron-hole recombination. Because the conduction band of TiO_2 is nearly isoenergetic with the reduction band potential of oxygen in inert solvents, adsorbed oxygen serves as a trap for the photogenerated conduction band electron in many heterogeneous photocatalytic reactions. It is often found that photocatalytic activity is nearly completely suppressed in the absence of

oxygen, possibly because of back interfacial electron transfer from active species present on the photocatalyst surface, and the steady-state concentration of oxygen has a profound effect on the relative rate of photocatalyzed decontamination occurring under ambient conditions. The resulting species, superoxide ' O_2^- ', is highly active and can attack either organic molecules or adsorbed intermediates or, after protonation, can provide another source for surface-bound hydroxy radicals. Its precise role has yet to be established unambiguously.

Oxygen concentration dependence has been explained as involving O_2 adsorption and depletion, both in the dark and during illumination, at the photocatalyst surface. That rutile possesses much lower photoactivity than anatase (despite the fact that both forms of TiO_2 are thermodynamically capable of reducing O_2) has been explained by the higher rate of electron-hole recombination on rutile because of its lower capacity to adsorb O_2 .

The superoxide (' O_2^- ') thus formed is an effective oxygenation agent, attacking both neutral substrates and surface-adsorbed radicals and/or radical ions. This attack occurs before desorption from the surface since the presence of dissolved superoxide traps in solution does not inhibit photocatalytic reduction-protonation sequence generates hydrogen peroxide, which can be decomposed on the photocatalyst surface to form hydroxy radical, which can also initiate oxidative functional group interconversions.