

CHAPTER II

LITERATURE REVIEWS

There have been several studies on the synthesis of titania and improvement of titania properties. A researcher has been found the advantage and drawback which not only the synthesis method but also in titania properties. Their works are very useful to apply titania in several ways such as, the photocatalytic reaction, electronic equipment, industrial etc. and learn to develop technical for modify and apply in the future.

Inoue *et al.* (1992) studied reaction of aluminium alkoxides with various glycols and the layer structure of their products. They synthesized alumina products by hydrothermal reaction of aluminium isopropoxide (AIP) in various glycol solvents, instead of water for hydrothermal synthesis, such as 1,4 butanediol (1,4 1,4-BG), 1,3 propanediol (1,3 PG) and 1,6 hexanediol (1,6 HG), which the products were amorphous or boehmite depended on type of glycol. When they prepared alumina products by different starting materials in 1,4 1,4-BG, found that the product had identical structure. In various glycols, they reported that the crystallite sizes increased with increasing carbon number and the products had the glycol moieties incorporation. They concluded that the glycol moieties were incorporated between the layers of boehmite resulting in enlargement of the basal spacing which the basal spacing of the product increased with increasing carbon number of the glycol. They found that a small amount of water may be present in the glycol sample and is possibly formed by thermal decomposition of glycol.

Ahuja *et al.* (1996) studied the influence of bulk and surface defects, which participate in the charge transfer process during photocatalysis and the effect of inorganic oxidizing species as electron scavengers on the rate of the photocatalytic degradation of phenol. Nanometre-sized powder of SrTiO_3 were prepared at 70-100°C by the wet-chemical method of gel to crystallite (G-C) conversion. The crystallite sizes obtained were in the range 5-13 nm, as estimated by transmission electron microscopy (TEM) studies. The photocatalytic activities of these powders in the

mineralization of phenol were evaluated in comparison with Degussa P25 (TiO₂). The maximum photocatalytic activity was observed for powders annealed in the range 1100-1300°C. The optical spectra of the particle suspensions in water showed broadened absorption around the band gap region, together with the appearance of an absorption maximum in the UV region.

Nakaoka *et al.* (1997) studied ESR Investigation into the effects of heat treatment and crystal structure on radicals produced over irradiated TiO₂ powder. Electron spin resonance measurements were carried out at 77 K under irradiation for anatase TiO₂ powders treated by heating at various temperatures in the air. For the untreated powder photoproducted holes were trapped at the surface forming Ti⁴⁺ O⁻ Ti⁴⁺-OH⁻ radicals, while, for the heated powder, they were trapped as Ti⁴⁺ O²⁻ Ti⁴⁺-O⁻ radicals at the surface. Photoproducted electrons were trapped as Ti⁴⁺ at the surface of the unheated powder, while they trapped at the inner part of the heat-treated powder. These differences could be explained by the desorption of surface hydroxyl groups and the change in the surface structure accompanied by the crystalline growth. No photoproducted radicals were detected for rutile TiO₂ powder, which may explain the low photocatalytic activity of this crystalline structure.

Yanggisawa *et al.* (1997) had synthesized anatase titanias were produced at low temperature below 350°C by hydrothermal hot-pressing of amorphous titania consisting of spherical particles prepared by hydrolysis of titanium tetraethoxide. They found that water included in the starting powder was released to produce hydrothermal conditions by heating and the hydrothermal treatment event at 100°C accelerated crystallization of the amorphous titania to anatase. In various temperature, the remarkable decrease in the surface area with the increase in reaction temperature from 100°C to 150°C indicated that a large amount of amorphous parts remained in the compacts produced at 100°C. In various reaction pressure, compressive pressure from outside the autoclave, the crystallite size did not change with varying reaction pressure, which suggested that the compression had no effect on the crystallization of anatase.

Kominami *et al.* (1997) used titanium (IV) tetra-tert-butoxide (TTB) to synthesize titania by thermal decomposition reaction in organic solvent at 573 K, the titania sample they prepared by this method will be called TD-TiO₂ (thermal decomposition). They found that TTB was completely decomposed at this condition that yielded anatase without contamination of any other phase. When they changed solvent (toluene) in this reaction, they found that TTB was decomposed in toluene even at 473 K to give anatase having quite large surface area. Since the BET surface area of a sample synthesized at 523 K was larger than that calculated from its crystalline size (they assumed the density of anatase to be 3.84 g cm⁻³), it suggested that the product synthesized at lower temperature were contaminated with the amorphous-like hydrated phase. In the effect of the structure of the alkyl group in the starting alkoxide, they found that primary and secondary alkoxides of titanium (IV) were not decomposed even at 573 K. This suggested that the process requires direct cleavage of the C-O bonds in alkoxides, and therefore the thermal stability of the C-O bond may be a decisive factor for the formation of TiO₂ lattice. When TiO₂ calcined the transformation had occurred to partly form rutile at 973 K and the loss of surface area by calcination was presumably because the as-prepared TiO₂ was well-crystallized having smaller tendency toward sintering and contained lesser amount of amorphous-like phase to be crystallized into anatase upon calcinations.

Yoshinaka *et al.* (1997) studied in a formation and sintering of TiO₂ (anatase) solid solution in system TiO₂-SiO₂. As-synthesized titania was prepared by hydrazine method, they had developed the new method using hydrazine monohydrate ((NH₂)₂·H₂O) in the hydrolysis reaction. The product was form anatase titania. When they added SiO₂ to synthesized titania, they found that transformation of anatase occurred at higher temperature with increased SiO₂ content and a linear decrease in specific surface area was due to the formation of tightly bound aggregated in the primary particles with increase temperature. In the transformation of anatase to rutile they suggest that anatase by transformation decomposed into rutile and amorphous SiO₂, no crystalline SiO₂ was recognized throughout the heating process.

Park *et al.* (1997) studied effect of solvent on titania particle formation and morphology in thermal hydrolysis of TiCl₄. They synthesized titania powder by thermal hydrolysis of titanium tetrachloride in mixed solvent of *n*-propanol and water.

They found that precipitates obtained with pure water were fine and highly agglomerated. They reported that a decrease in the dielectric constant of the solution promotes the precipitation of titania by reducing the solubility of the titania in the solvent and promotes the supersaturation of titania in the solvent. In addition, they found that morphologies of titania depended on particle surface potential and the dielectric constant which the magnitude of the energy barrier and maximum repulsive force was determined mainly by them. In nucleation, they reported that the particle growth after nucleation could be also effect by the kinds of solvent, because the particle interaction potential is different in each solvent. They proposed the particle growth in three ways mechanism of agglomerate of secondary particles (Figure 2.1).

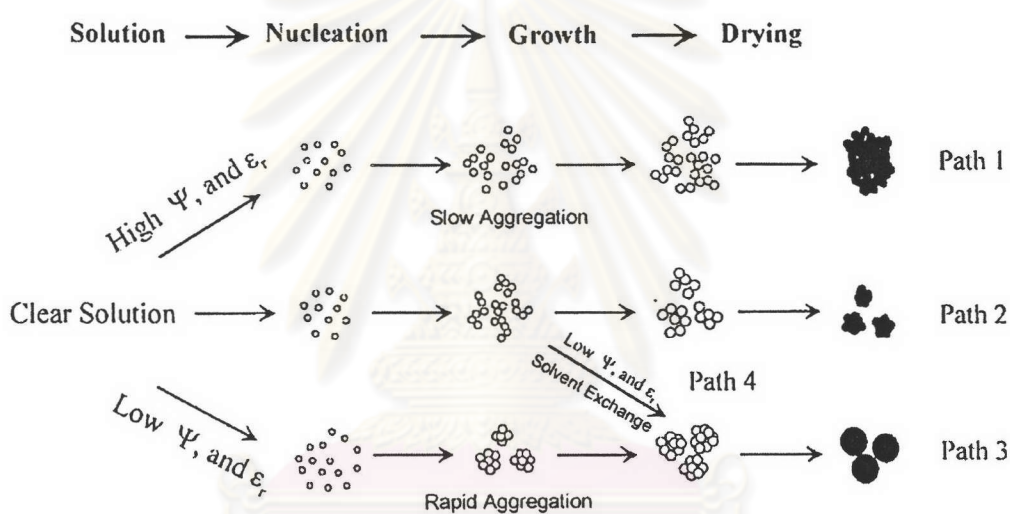


Figure 2.1 Schematics of particle growth in the mixed solvent of alcohol and water. (Park *et al.*, 1997)

In some previous work found that washing powder (starting material of ceramic material) with organic solvents is an effective way of avoiding the formation of hard agglomerates. It is proposed that agglomerate strength is determined by the extent to which water molecules, hydrogen-bonded to surface hydroxyl groups, are able bridges between adjacent particles. Organic solvents can remove hydroxyl groups and water and leads to reduction and/or elimination of hard agglomerates [Readey *et al.* (1990); Kaliszewaki *et al.* (1990)]. Yin *et al.* (1998) studied crystallization of titania in liquid media and photochemical properties of crystallized titania. They prepared titania from titanium tetraisopropoxide in *i*-propanol that

derived amorphous TiO₂ gel. When heat treatments of the gels in water, *n*-hexane and methanol crystallization occurred above 120 °C which the rate of crystallization was in the order in water > *n*-hexane > methanol. On the other hand, they studied in the crystallization behavior of the gels in methanol-water and *n*-hexane-water mixed solutions found that the rate increased with increased water fraction. The results suggested that water is essential for crystallization of gel and that the crystallization proceeded via a dissolution-reprecipitation mechanism, where the gel dissolves as hydrated ions by reaction with water absorbed on the surface.

Inoue *et al.* (1998) studied glycothermal synthesis of rare earth iron garnets. They synthesized iron oxide products by glycothermal synthesis, the use of organic media in place of water for the hydrothermal method, in 1,4 butanediol. They reported that in the glycothermal reaction, thermal decomposition of the glycol moiety is directly connected with the crystallization of the products, and therefore starting materials with a high energy level provide a large driving force for the formation of the products. They explained that because of the large driving force available in the glycothermal reaction, crystal growth proceeds rapidly even though the lattice parameter of the grown crystals is much larger than that of the seed crystals. So that, the lattice strain caused by the epitaxial growth of a new crystal on a seed crystal having different lattice parameters is released by edge dislocations and the creation of a number of crystal defect is another characteristic of the glycothermal method. In the same year, Inoue *et al.* (1998) studied reactions of rare earth acetates with aluminum isopropoxide (AIP) in ethylene glycol. They found that modified-alumina had synthesized by glycothermal method derived amorphous and/or crystal. They reported that a formation of the amorphous product in the reaction can be interpreted by the difficulty in the cleavage of the C-O bond of the intermediate glycoxide formed by the reaction of AIP with ethylene glycol, where the ease in the cleavage of the C-O bond seems to be the prime factor for the formation of crystalline garnets by the reaction in 1,4 1,4-BG.

Jung *et al.* (1999) studied preparation anatase-phase titania by embedding silica and photocatalytic activity for the decomposition of trichloroethylene. Nanophase titania particles were prepared by the sol-gel process using two different precursors; titanium isopropoxide(TTIP) and titanium ethoxide (TEOT). Silica-

embedded titania particles was also prepared from TEOT and tetra-ethyl-ortho-silicate (TEOS). In the case of nanophase titania particles prepared from TTIP, the rutile/anatase mixed phase had higher photoactivity than the pure anatase in the decomposition of TCE. However, in the nanophase titania prepared from TEOT, the photoactivity was increased with the heat treatment temperature until rutile phase began to be formed. The surface area was decreased with the heat treatment temperature. The photoactivity of the pure anatase titania prepared from TEOT was higher than that of Degussa P25 and the anatase/rutile mixed titania prepared from TTIP. Therefore, we concluded that, in order to achieve high photocatalytic activity, it was important to prepare titania particles at high temperature, preferably without forming rutile phase but not necessarily. This conclusion was confirmed by the experimental result that the silica-embedded titania particle of pure anatase phase had higher photoactivity than that of Degussa P25 and the pure anatase titania prepared from TEOT. The embedding of small amount of silica into anatase titania matrix enhanced the thermal stability of nanophase titania particle resulting in the suppression of the phase transformation from anatase to rutile phase. This thermal stability enables us to calcine the silica-embedded particles at higher temperature without accompanying the phase transformation and to reduce the bulk defects, which are responsible for the low photocatalytic activity.

Kominami *et al.* (1999) has synthesized titania by hydrolyzed titanium alkoxide (titanium *n*-butoxide, TNB) in organic solvents at high temperatures and developed novel method, i.e., hydrolysis of titania alkoxides with water homogeneously formed from alcohols used as the solvent. The titania sample prepared by the novel method was called THyCA (Transfer Hydrolytic Crystallization in Alcohols) TiO₂. The products prepared by this method was anatase with out contamination of any other phase such as rutile or brookite and the products contained a negligible amount of amorphous-like phase. In the effect of synthesis condition on the physical properties of THyCA-TiO₂, they prepared THyCA-TiO₂ under various conditions such as vary alkoxide or vary alcohol. The reaction of TNB in 2-propanol, microcrystalline titania was formed at 548 K while reaction at 523 K gave no solid product, indicating that dehydration of 2-propanol required temperature higher than 523 K, when titanium isopropoxide (TIP) was dissolved in a mixed solvent of 2-propanol in toluene TIP was completely hydrolyzed to give anatase titania. When

calcination on THyCA-TiO₂ prepared in the TNB-2-propanol, phase transformation of anatase occurred at 1173 K that induced partial transformation onto the rutile. The high thermal stability of THyCA-TiO₂, they assumed that the as-prepared THyCA-TiO₂ consisted of single crystals and contained negligible amount of amorphous-like phase to be crystallized into anatase and to induced sintering of crystallites upon calcination. In the same year, Kominami *et al.* (1999) studied new synthesis method for nanosized by hydrolysis of titanium *n*-butoxide (TNB) in toluene and add water in the gap of autoclave. During the reaction, water in the gap was vaporized, dissolved in toluene from the gas phase, and hydrolyzed TNB. Titania was prepared in various conditions, found that anatase and amorphous formed in the reaction. When they calculate surface area in assumption that the particles were nonporous spheres for compared the specific surface area from BET measurement which test contaminate amorphous phase in the as-prepared titania. They found that when the reaction time was prolonged, the crystallite size was gradually increased and the effect of the combustion heat of the organic moieties locally raises the surface temperature of crystals, which can accelerate the crystallization and/or sintering of TiO₂ crystals (or particle) from the calcinations and the decrease in surface area from BET was probably due to sintering of single crystals.

Kin *et al.* (1999) studied homogenous precipitation of titania ultrafine powder from aqueous TiOCl₂ solution. They found the as-precipitated hydroxide was amorphous at first and became crystalline as the heat-treatment temperature increased and found that the precipitation was not determined by the heating rate but by heating temperature and time. They reported that the homogenous precipitation method using simple heating produced nanosized crystalline powder. In agglomeration of primary particle, they found the increased agglomeration or growth of TiO₂ primary particle with increased in thermal energy in the reaction.

Jung *et al.* (1999) studied enhanced photocatalytivity of silica-embedded titania particles prepared by sol-gel process. They found that the major phase of the silica-titania particles prepared by sol-gel technique was pure anatase without other contamination phase and silica crystal. They reported that the added silicon formed segregated amorphous silica and embedded into anatase titania matrix which affect the increase of thermal stability result in suppressing the phase transformation from

anatase to rutile, in addition, the degree of aggregation of primary particles decreased with increasing the silica content.

Takeda *et al.* (2001) studied photocatalytic TiO₂ thin film deposited onto glass by DC magnetron sputtering. A high performance photocatalytic TiO₂ thin film was successfully obtained by reactive DC magnetron sputtering. The film was deposited onto SiO₂-coated glass at a substrate temperature of 220°C using a titanium metal target in O₂ 100% atmosphere. The film showed good uniformity of thickness in a large area with the optical transmittance of ~80% in the visible region. The decomposition ability of acetaldehyde (CH₃CHO) of the film under UV irradiation was almost the same as that of the sol-gel-derived TiO₂ thin film but the sputtered film showed a much higher mechanical durability. The characterization of the films was carried out using XRD, SEM, AFM, XPS and SIMS, and the electronic structures of the films were calculated using a first-principle calculation method based on the density functional theory. It was found that the amount of incorporated ¹⁸O into the film was larger for the films with lower photocatalytic activity when the films were annealed in ¹⁸O₂/N₂ atmosphere. This result indicates that the amount of oxygen vacancies, which were occupied by incorporated ¹⁸O, was larger for the films with lower photocatalytic activity. Furthermore, the introduction of structural defects associated with oxygen vacancies was found to create some energy levels around the mid-gap, indicating that they could work as recombination centers of photo-induced holes and electrons, causing the decrease in photocatalytic activity. Therefore, the decrease in the structural defects associated with oxygen vacancies is important for improving the photocatalytic activity of the films.

Zhang *et al.* (2001) controlled the temperature of the hydrolysis of titanium ethoxide to synthesize nanocrystalline and amorphous titania. By heating the amorphous titania in air at 375 °C to 550 °C for 3 h, single-phase anatase powders were prepared. They had varied condition (synthesized at 0 °C for 3h, large amount batch at 0°C, at 50 °C for 3 h, at 70 °C for 3 h) for synthesize titania and found that at T > 375 °C for pure amorphous titania, single phase anatase can be generated from amorphous titania after heating for only 3 h or less. By heating various starting materials at different temperature for 3 h, they found that the average size of anatase depends on the history of the starting material because the material history can effect

the transformation kinetics and thus the average particle size. Anatase particles formed by heating of the amorphous titania were spherical. They concluded that large anatase particles may have grown by one of three pathways. First, large anatase particles may form directly from aggregates of smaller amorphous titania particles. Second, large anatase particles may grow by atom-by-atom recrystallization of smaller anatase particles. Third, large anatase crystals may form by solid-state aggregation of adjacent small anatase particles as the crystals adopt appropriate crystallographic orientations.

Iwamoto *et al.* (2001) studied preparation of the xerogels of nanocrystalline titania by the removal of the glycol at the reaction temperature after the glycothermal method and their enhanced photocatalytic activities. They synthesized titania products by titanium tetraisopropoxide (TIP) and an appropriate amount of tetraethyl orthosilicate (TEOS) were added to 100 ml of 1,4-butanediol at 300°C and kept at that temperature for 2 h (glycothermal method), in the second method, after the glycothermal reaction, removed the organic vapor from the autoclave by flash evaporation while keeping at 300°C and its products formed anatase titania with non-contamination of other phase or amorphous phase. In second method, when increasing in the amount of the TEOS addition the crystallite size decrease which they reported that the crystallization mechanism was not effected by the removal of the glycol at the reaction temperature. In the other hand, the removal of the glycol at the reaction temperature, the titania product (without TEOS in the reaction) had improvement of the thermal stabilities. In addition of TEOS in the reaction both of the method, the temperature transformation had shift, they reported that the silica-modification of titania had been improve thermal stability both of the methods. They found that the products, synthesized from second method, were the collapse of the coagulated structure indicated that coagulation during drying of wet gels due to the surface tension of the liquid.

Li *et al.* (2002) studied investigates the mechanism of photosensitization and the recombination of excited electron-hole pairs affected by depositing platinum (Pt) on the surface of titanium dioxide (TiO₂). A new catalyst of Pt-TiO₂ was prepared by a photoreduction process. Being model reactions, the photocatalytic oxidation of methylene blue (MB) and methyl orange (MO) in aqueous solutions using the Pt-TiO₂ catalyst was carried out under either UV or visible light irradiation. The

experimental results indicate that an optimal content of 0.75%Pt–TiO₂ achieves the best photocatalytic performance of MB and MO degradation and that the Pt–TiO₂ catalyst can be sensitized by visible light. The interaction of Pt and TiO₂ was investigated by means of UV–Vis absorption spectra, photoluminescence emission spectra, and X-ray photoelectron emission spectroscopy. The Pt⁰, Pt²⁺ and Pt⁴⁺ species existing on the surface of Pt–TiO₂, and the Ti³⁺ species existing in its lattice may form a defect energy level. The Pt impurities, including Pt, Pt(OH)₂, and PtO₂, and the defect energy level absorb visible light more efficiently in comparison with the pure TiO₂ and hinder the recombination rate of excited electron–hole pairs.

Hirano *et al.* (2002) studied direct formation of zirconia-doped titania with stable anatase-type structure by thermal hydrolysis. They found that the ZrO₂ content in the starting solution increased, a shift of the diffraction peak of the as-precipitated anatase-type TiO₂ to lower diffraction angle was observed. In heat treatment, they found a small amount of tetragonal ZrO₂ was detected after heat treatment at >950°C and the anatase structure was fully maintained when ZrO₂ was doped in the titania, even after heat treatment at 1000°C. They reported that the hydrothermally precipitated anatase particles with nanosized crystallites can produce solid solution with large amount of ZrO₂ than those with high crystallinity and large crystallite size after heat treatment at 950° - 1000°C.

Kominami *et al.* (2002) studied synthesis of perovskite-type lanthanum iron oxide by glycothermal reaction of a lanthanum-iron precursor. They prepared the precursor by reacted a mixture of lanthanum (III) isopropoxide (LIP) and iron (III) *n*-bitoxide (INB) in toluene, this process in toluene they call the solvothermal decomposition process and they used the precursor reacted in 1,4 butanediol (1,4-BG), this solvothermal process in 1,4-BG is called a glycothermal process. Formation of the amorphous phase that prepared by solvothermal decomposition of the mixture of LIP and INB in toluene, they found that it suggested a relatively strong interaction between two starting compounds and high homogeneity of lanthanum and iron species in the precursor. When they prepared the product by direct glycothermal reaction of a mixture of LIP and INB without preparation of the precursor using the solvothermal decomposition process they found that the starting materials, LIP and

INB, reacted independently under glycothermal condition and yielded each related compound.

Lee *et al.* (2003) studied photocatalysis and hydrophilicity of doped TiO₂ thin films. TiO₂ thin films were prepared using the dip-coating method with a polymeric sol including additives such as Al, W, and Al + W to examine two major properties: photocatalysis and hydrophilicity. W-doped films showed the best photocatalytic efficiency, while Al-doped film was poorer than undoped samples. However, good hydrophilicity in terms of saturation contact angle and surface conversion rate was found in Al- and (Al + W)-mixed-doped films. It was found that deep electron-hole traps and high surface acidity of W-doped TiO₂ thin film were the major factors in high photocatalytic efficiency. In addition, low surface acidities of Al- and (Al +W)-doped films provided better hydrophilicity than W-doped ones. However, the amount of [Ti³⁺] point defects on the surface was another major factor, probably the most important, in getting the best hydrophilicity. Conclusively, it seemed that many parts of the photocatalysis mechanism depend more on bulk-related properties than do those of hydrophilicity, which can be defined as an interfacial (surface) or near-surface-restricted process.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย