

CHAPTER II

LITERATURE REVIEWS

There are many methods for titanium (IV) oxide synthesis. However, only a few papers have dealt with the synthesis by hydrothermal or glycothermal method. These methods have the advantages that the products consist of microcrystalline particles but are sufficiently high thermal stability. They are also highly active for the photodegradation of organic compounds.

2.1 Reviewed Papers

In this section, the relevant the synthesis titanium (IV) oxide using organic solvents, photocatalytic oxidation of several substances by titanium (IV) oxide, and effects of parameters of catalyst preparation on the catalytic oxidation of organic substances are summarized to raise the problem issue. They are as follows:

Kominami et al. (1996) examined the synthesis of thermally stable nanocrystalline anatase by high temperature hydrolysis of titanium alkoxide with water dissolved in organic solvent from gas phase. They found that when the reaction was carried out at 125°C for 2 hr, Titanium normal butoxide, TNB, was not hydrolysed. But anatase was formed as the sole product at temperatures higher than 150°C. The crystallite size of the anatase formed gradually increased with increasing reaction temperature and prolonged reaction time. In addition, the physical properties, such as crystallite size, pore size and pore volume, can be controlled by reaction conditions and the choice of organic solvents.

Kominami et al. (1997) focused on synthesis of microcrystalline titanium (IV) oxide by thermal decomposition of titanium tetra-tert butoxide, TTB, in inert solvents at 300°C. It was found that the product yielded microcrystalline anatase titanium (IV) oxide powders with a crystallite size of ca. 9 nm and a surface area of $> 100 \text{ m}^2 \text{ g}^{-1}$. Primary and secondary alkoxides of titanium (IV), however, were not decomposed under similar conditions, indicating that the thermal stability of C-O bonds in the

alkoxides was a decisive factor for their decomposition. The as-prepared titanium (IV) oxide powders, without calcination, exhibited much higher rate of carbon dioxide formation than any other active photocatalysts such as Degussa P-25 and Ishihara ST-01 in the photocatalytic mineralization of acetic acid in aerated aqueous solutions. The higher activity of the present TiO₂ photocatalysts was attributed to both high crystallinity and large surface of the present product. The calcination of the as-prepared TiO₂ in air reduced the photocatalytic activity, but it was still higher than the other commercially available TiO₂'s. In addition, the photoactivity of as-prepared TiO₂ catalyst increases with crystal size increasing from <5 to 9 nm.

Kominami et al. (1998) studied a new preparation process allowing compatibility of high adsorptivity and low electron-hole recombination probability. They found that in a photocatalytic reaction system of silver metal deposition, upon elevating the post-calcination temperature, the photocatalytic activity was enhanced in spite of the simultaneous decrease in amount of surface-adsorbed Ag⁺.

Mendez-Roman and Cardona-Martinez (1998) investigated the relationship between the formation of surface species and catalyst deactivation during the gas phase photocatalytic oxidation of toluene by using in situ FTIR spectroscopy. They identified benzaldehyde and benzoic acid on the surface of the deactivated photocatalysts. Additional GC/MS analysis of methanol-extracted surface species confirmed the presence of benzaldehyde and benzoic acid and detected small concentrations of benzyl alcohol. Apparently, benzaldehyde was the main partial oxidation product that was further oxidized to benzoic acid. Benzoic acid was strongly adsorbed on the surface of the catalyst. The presence of gas phase water in the reactive mixture seemed to retard the formation of benzoic acid. In the complete absence of water vapor, the catalyst photo-oxidation activity rapidly declined with time on stream. When water was present in the reactive mixture the decrease in activity was slower. Catalyst activity might be completely or partially recovered (depending on the reactive system) by flowing humid air over the catalyst in the presence of UV illumination.

Zhang and co-workers (1998) investigated the role of particle size in nanocrystalline TiO₂-Based photocatalysts. It was exhibited that particle size was a crucial factor in the dynamics of the electron/hole recombination process. For TiO₂ particles with 6 or 11 nm diameter, Fe³⁺ dopants were added to inhibit the charge carrier surface recombination. In addition, the photocatalytic efficiency of TiO₂ did not monotonically increase with decreasing particle size, and there existed an optimal particle size of about 10 nm for the liquid-phase decomposition of chloroform.

Cao et al. (1999) investigated the effects of preparation methods, humidity, and calcination temperatures on the behavior of nanoscale TiO₂ photocatalyst in the gas phase decomposition of 1-butene. Their experimental results revealed that oxidation rates of 1-butene decreased exponentially with increasing water concentrations in the flowing stream. However, a trace amount of water vapor was indispensable in maintaining the stability of the catalysts. Proper calcination temperature (300°C) could promote the resistance of catalysts against the poisoning effects of humidity. For the catalyst characterization, XRD patterns and BET measurements indicated that moderate surface areas (from 100 to 160 m² g⁻¹), appropriate crystallite sizes (5~6 nm), and crystallinity of anatase were beneficial to the photoactivity of TiO₂ catalysts. In the reaction of oxidizing 1-butene, water played two different roles, as a stabilizer by replenishing hydroxyl groups at low humidity, and as a strong inhibitor by competing with 1-butene for adsorption of active sites.

Kominami et al. (1999a) discussed the effect of the reaction conditions on the properties of formed TiO₂ synthesized by hydrolysis of titanium (IV) alkoxide in toluene with water that was dissolved from the gas phase. They found that with elevation of the reaction temperature and an increase of the reaction time, the crystallite size of the anatase was gradually increased from ca. 7 nm to ca. 20 nm in the present reaction medium. Corresponding to the crystal growth, surface areas of the products were decreased while the rutile-transformation temperature became higher and the thermal stability was improved.

Kominami and co-workers (1999b) intended to hydrolyze titanium alkoxide more homogeneously in organic solvents at high temperature and developed a novel method, i.e., hydrolysis of titanium alkoxides with water homogeneously formed from alcohols used as the solvents. They reported that reaction in other 2-alkanols, 1-alkanols except ethanol, and tert-alkanol yielded also microcrystalline anatase TiO_2 as in the case of 2-butanol, showing that all alcohols except ethanol used in this work undergo dehydration to liberate water under the autoclaving conditions. The autogenous pressure during the reaction depended on the kind of alcohol. Therefore, anatase particles of various crystallite size (11-31 nm) and surface areas ($42\text{-}138\text{ m}^2\text{ g}^{-1}$) could be synthesized. The TiO_2 samples prepared by this method are called THyCA (Transfer Hydrolytic Crystallization in Alcohols) TiO_2 .

Photocatalytic activity of THyCA- TiO_2 strongly depended on the alcohols used in the synthesis procedure. TiO_2 samples prepared in alcohols of smaller carbon numbers tended to exhibit higher activity. In addition, the higher pressure seems to improve the crystallinity of anatase, leading to the decrease in the surface defects and thereby the increase in photocatalytic activity.

Marta et al. (1999) discussed the role of H_2O in the photocatalytic oxidation of toluene in vapor phase on anatase TiO_2 catalyst. This reaction has been carried out in a fixed-bed continuous reactor. Air containing toluene and water vapor in various water ratios was fed to the photoreactor irradiated by a medium pressure Hg lamp. Toluene was mainly photo-oxidized to benzaldehyde, and small amounts of benzene, benzyl alcohol and traces of benzoic acid and phenol were detected. In the presence of water, no decrease of photoreactivity was observed at steady state conditions. By removing water vapor from the feed, the conversion of toluene to benzaldehyde was almost completely inhibited, and an irreversible deactivation of catalyst occurred. FTIR experiments carried out in model conditions indicated that the layer of surface OH groups was kept essentially uncharged under UV irradiation in the presence of H_2O vapor, whereas it was irreversibly depleted by exposure to the UV light in dry conditions. As surface hydroxyls were needed to photo-oxidize toluene to

benzaldehyde, this might be the origin of the almost complete and irreversible depletion of the toluene conversion by using a dry reaction mixture.

Park and co-workers (1999) focused on the photocatalytic oxidation of ethylene to carbon dioxide and water on ultrafine powdered TiO₂ photocatalysts in the presence of oxygen and water. The results suggested that the addition of water enhance the photo-oxidation reaction. The large surface area of the photocatalyst was one of the most important factors in achieving a high efficiency in the photocatalytic oxidation of ethylene. The photo-formed OH species as well as O₂⁻ and O₃⁻ anion radicals played a significant role as a key active species in the complete photocatalytic oxidation of ethylene with oxygen into carbon dioxide and water. Anatase TiO₂ with a large surface area, large band gap, and numerous OH groups was more efficient for the oxidation of ethylene. The increased band gap was accompanied by a shift in the conduction band edge to higher energies. This moves the reductive potential to more negative values and enhanced the photocatalytic reactivity.

Xu et al. (1999a) discussed the preparation and characterization of TiO₂ ultrafine particles. The TiO₂ ultrafine particles were prepared by means of the colloidal chemical method. The structure and properties of the as-prepared TiO₂ were studied using TEM, XRD, IR, XPS, and UV-vis absorption spectrum. The results suggested that the surface photoactivity for a TiO₂ powder was proportional to the number of surface active species such as hydroxyl groups and Ti³⁺ which could improve the photocatalytic activity of TiO₂.

Xu et al. (1999b) discussed the effects of particle size of TiO₂ on photocatalytic degradation of methylene blue, MB, in aqueous suspensions. The results suggested that the adsorption rate and adsorbability of MB on suspended TiO₂ particles increased as the particle size of TiO₂ became smaller, especially when the particle size is less than 30 nm. The half-life of the photocatalytic degradation of MB also decreased as the particle sizes of TiO₂ decreased. Additionally, photocatalytic activity tended to increase as the crystal size of titanium (IV) oxide catalyst decrease.

Photocatalytic activity monotonically increased with crystal size decrease from 49 to 0.03 micrometer.

Cao et al. (2000) studied photocatalytic oxidation of toluene on nanoscale TiO₂ catalysts in case of deactivation and regeneration. It was shown that nanoscale TiO₂ catalysts prepared using a sol-gel method exhibit higher initial activity than commercially available Degussa P-25 TiO₂ for the photocatalytic oxidation of toluene. Unlike Degussa P-25 TiO₂, nonporous, nanoscale TiO₂ catalysts were composed mainly of mesopores with pore sizes in the range of 35-44 nm. Results of competitive adsorption of water and toluene on TiO₂ samples confirmed that TiO₂ had a highly hydrophilic surface, which intrinsically suppressed the oxidation rate of toluene at high water content in the feed stream. Severe deactivation of TiO₂ catalysts was due to the accumulation of partially oxidized intermediates, such as benzaldehyde and benzoic acid, on active sites. Kinetic studies of the deactivation process indicated that the adsorption of poisonous intermediates in the initial stage of the photocatalytic reaction was almost irreversible. The initial oxidation rates on the catalysts were proportional to their surface areas.

Kozlov et al. (2000) demonstrated gas phase ethanol photocatalytic oxidation on the series of TiO₂ samples by the FTIR in situ method. TiO₂ samples were prepared by the hydrolysis of TiCl₄ under different pH, followed by annealing at 400°C for 1 hr. They found that the TiO₂ samples possessed similar physicochemical properties (porosity, specific area), but were found to have different photocatalytic activities because the stability of the carboxylate species increased as the surface acidity decrease. The lower the acidity of TiO₂ surface, the stronger was the interaction of carbon acids with it to form the carboxylate structures which form during the VOCs photo-oxidation. These carboxylate structures occupied the surface sites preventing further interaction of the gaseous reagents with the catalyst surface.

Maira and co-workers (2000) investigated the size effects in gas phase photo-oxidation of trichloroethylene, TCE, using nanometer-sized TiO₂ catalysts. They found an enhancement in the rate of TCE conversion as the TiO₂ crystal size

decreased from 27 to 7 nm. However, the catalyst activity dropped when smaller TiO₂ particles (i.e., 3.8 and 2.3 nm) were used. The results suggest that an optimum TCE degradation can be obtained from catalyst with 7-nm TiO₂ crystals.

Zhang and co-workers (2000) focused on effects of calcination on the photocatalytic properties of nanosized TiO₂ powders prepared by TiCl₄ hydrolysis. It was exhibited that calcination was an effective treatment to increase the photoactivity of nanosized TiO₂ photocatalysts resulting from the improvement of crystallinity. But after calcination at 600°C, the photoactivities of these catalysts decreased significantly, since semiconductors in larger size resulted in the recombination of photogenerated holes and electrons at higher rate. Additionally, mixtures of both phases exhibited higher photoactivity as well as effective degradation in comparison with pure anatase or rutile catalysts.

2.2 Comments

From the above reviewed literature, it can be seen that there are many researches studied various effects of catalyst preparation parameters on the photocatalytic oxidation of organic compound by using the TiO₂ catalyst. However, effects of crystal size of TiO₂ photocatalyst are not widely investigated and relationship between the crystal size and photocatalytic activity of TiO₂ is ambiguous [Kominami et al. (1997), Zhang et al. (1998), Xu et al. (1999b), and Maira et al. (2000)]. Therefore, it is an interesting point to study the crystal size effects of TiO₂ catalyst on gas phase photo-oxidation of organic compounds.

There are many methods of titanium (IV) oxide synthesis used for the photocatalytic reaction. Glycothermal method is the one of the process for titanium (IV) oxide synthesis. The titanium (IV) oxide synthesized by glycothermal method can have different physical and chemical properties, such as crystal size, surface area, thermal stability) depend on the parameter synthesis. Therefore, in this thesis we use titanium (IV) oxide synthesized by glycothermal method for determining the crystal size effect on the gas phase photo-oxidation of 2-propanol.