

CHAPTER II

LITERATURE REVIEWS

Campbell et al [1992] synthesized a high-surface-area TiO_2 aerogel by optimizing the water and acid contents in the sol-gel synthesis using a methanolic solution of titanium n-butoxide. Low-temperature aerogel was dried by semicontinuous extraction with supercritical CO_2 at 343 K and 20.7 MPa. The uncalcined titania aerogels were amorphous up to a calcination temperature of 673 K and were transformed from anatase into rutile phase in the temperature range of 873-1073 K. The aerogel had specific surface areas of up to $650 \text{ m}^2/\text{g}$ and specific pore volumes of up to $2.1 \text{ m}^3/\text{g}$. The pore size distribution ranged from 2 to 10 nm at a temperature lower than 873 K.

Dagan and Tomkiewicz [1994] synthesized titania aerogel. The molar ratio of alkoxide to nitric acid was kept constant at 1: 0.08, whereas the alcoholic solvent and water concentrations were varied. Prior to supercritical drying, the gel was washed with excess fresh alcohol or water. The non-annealed aerogels possessed BET surface area of up to $600 \text{ m}^2/\text{g}$ and were mesoporous. Annealing at 673-773 K led to a drop in BET surface areas to less than $190 \text{ m}^2/\text{g}$. The photoassisted oxidation of salicylic acid on these materials was compared to that obtained with commercial (P25) TiO_2 powder. The aerogel shows a much higher photocatalytic activity

Song and Pratsinis [2000] studied the effect of solvent on properties of bimodal porous titania powders. TiO_2 powders were made by hydrolysis of titanium tetraisopropoxide (TTIP), which was dissolved in various alcohols (methanol, ethanol, isopropanol, and sec-butanol) with the alcohol/TTIP ratio in the range of 0-40. At excess alcohol concentration, the specific surface area (SSA) and the pore volume decreased in the order of sec-butanol, iso-propanol, ethanol, and methanol at constant alcohol/TTIP molar ratio. When TTIP was dissolved in ethanol, the molar ratio of ethanol/TTIP was varied in the range of 0-40. The dried powder made in ethanol contained more organic residue due to the TTIP molecules in ethanol were more diluted and the hydrolysis of TTIP was inhibited. The amount of residual alkyls prevented crystallization of TiO_2 to anatase. When TTIP was dissolved in methanol, a

precipitate was produced since the alcoholysis reaction produced titanium isopropoxy methoxide, which was insoluble in methanol. However, the precipitate was not produced in other alcohols.

Tursiloadi et al [2006] prepared TiO_2 aerogel from hydrolysis of titanium n-butoxide in methanol with acid catalyst, followed by CO_2 supercritical extraction. TiO_2 xerogel that was dried under an atmospheric pressure was also prepared for comparison. The weight loss of the xerogel (ca. 38%) in the temperature range up to 600°C is more than two times larger than that of the aerogel (ca. 17%) in the temperature range up to 450°C . The organic residues in the aerogel could be eliminated at a temperature (about 450°C) lower than those in the xerogel. During heating, the organic residues could be removed easily through the larger open pores of the aerogel. The anatase phase was found in the as-synthesized aerogel. On the contrary, the xerogel dried at 90°C was amorphous and underwent crystallization at 500°C . After calcination at 500°C , the specific surface area of the aerogel, about $90\text{ m}^2\text{ g}^{-1}$, was two times larger than that of the xerogel. After calcination at 600°C , the specific surface area of the xerogel drastically decreased, but that of the aerogel remained large at about $60\text{ m}^2\text{ g}^{-1}$.

Kolen'ko et al [2005] synthesized nanocrystalline (14-18 nm) by a sol-gel method, followed by supercritical drying in isopropanol (NI) or carbon dioxide (NA). Titanium tetraisopropoxide was used as precursor was dissolved in absolute ethanol with nitric acid. After supercritical drying, thermal treatment of the sample was carried out at 450 , 500 , and 550°C to remove organic residue. Supercritical drying of TiO_2 in isopropanol without thermal treatment led to the formation of anatase. The thermal treatment of NI was not necessary for crystallization. However, in the case of NA, the thermal treatment was necessary not only to burn organic compounds but also the increase in crystallinity. High temperature supercritical drying produced crystallized powder, which can be used in photocatalysis without additional thermal treatment. Photocatalytic results indicated that the sample dried in supercritical isopropanol possessed higher photocatalytic activity than that dried in CO_2 because of better electronic and surface properties.

Chen et al [2006] prepared TiO_2 by a facile epoxide sol-gel synthesis, followed by supercritical drying (aerogel) or direct drying (xerogel). The as-obtained aerogel and xerogel samples were calcined at a temperature ranging from 400-700 °C. From XRD patterns, both aerogel and xerogel were completely amorphous. After calcination in air at 400 °C, both aerogel and xerogel samples exhibited well-defined diffraction peaks that were characteristic of anatase phase. Comparison of the diffraction peaks of titania in these samples indicated that the diffraction peaks of anatase for the aerogel samples was broader and lower than those for the xerogel that was calcined at the same temperature. This result suggested that a much smaller anatase crystals were produced in the aerogel sample. As-synthesized aerogel ($464 \text{ m}^2\text{g}^{-1}$) possessed almost twice as much surface area as as-synthesized xerogel ($276 \text{ m}^2\text{g}^{-1}$). After calcination, the specific surface area of all aerogel was much higher than xerogel at similar calcination temperature. The aerogel sample still possessed a large surface area of $64 \text{ m}^2\text{g}^{-1}$ when being calcined at 600 °C. The photocatalytic degradation of phenol was used to evaluate the photocatalytic activities of aerogel and xerogel samples. The photocatalytic activity of the aerogel sample was much higher than that of xerogel due to a higher surface area and more effective control of the crystallite size and nanocrystalline phase.

Liu et al [2006] synthesized TiO_2 with high surface area and small crystallite size by hydrolysis Titanium tetraisopropoxide in pure water at 25 °C (T25) or 70 °C (T70), followed by drying at 100 °C. The as-prepared T70 xerogel appeared to be crystalline and showed obvious diffraction peaks of anatase and brookite phases. However, the as-prepared T25 xerogel was amorphous. The amorphous wet gel that was heated to 100 °C was amorphous. This result suggested that the higher hydrolysis temperature (70 °C) promoted the phase transition and crystallization of amorphous TiO_2 wet gel. This was probably due to the residual alkyls preventing crystallization to crystalline anatase. T70 sample possessed a very large specific surface area ($750 \text{ m}^2\text{g}^{-1}$) and a very high porosity (75.6%), which was higher than that of T25 (a specific surface area of $301.1 \text{ m}^2\text{g}^{-1}$ and a porosity of 63.5 %). This was attributed to the fact that T25 contained more unreacted alkyls, which blocked the pores in the T25 samples. The photocatalytic activities of T25, T70 and P25 were evaluated by the photocatalytic oxidation of acetone in air. T25 showed very low photocatalytic

activity due to contained amorphous. T70 showed high photocatalytic activity, which was slightly higher than that of P25. This may be attributed to a very large specific surface area and smaller crystallite size. Usually, the specific surface area and crystallite size of P25 are about $50 \text{ m}^2 \text{ g}^{-1}$ and 30 nm, respectively.

Yu et al [2006] prepared titania nanotube via a hydrothermal treatment of TiO_2 powders (P25) in a 10M NaOH solution at $150 \text{ }^\circ\text{C}$ for 48 hours, followed by calcination at and then calcined at various temperatures ($300\text{-}900 \text{ }^\circ\text{C}$). The photocatalytic activity of the nanotubes after calcination was evaluated by photocatalytic oxidation of acetone in air. The results indicated that at 400 to $600 \text{ }^\circ\text{C}$, the calcined nanotube samples showed a higher photocatalytic activity than Degussa P25. Especially, at 400 and $500 \text{ }^\circ\text{C}$, the photocatalytic activity of the calcined nanotubes exceeded that of P25 by a factor of 3. This could be attributed to the fact that the former had a larger specific surface area and a larger pore volume. With a further increase in the calcination temperature from 700 to $900 \text{ }^\circ\text{C}$, the photocatalytic activity of the calcined nanotube samples greatly decreased due to the formation of rutile phase, the sintering and growth of TiO_2 crystallites, and the decline in specific surface area and pore volume.

He and Lin et al [2007] compared properties and photocatalytic activities of various TiO_2 which, was dried under different conditions and were calcined at a temperature in the range of $400\text{-}1000 \text{ }^\circ\text{C}$. TiO_2 was synthesized by hydrolysis of TiCl_4 with 2.5% aqueous ammonia. The obtained wet gel was dried under two drying conditions. One was dried at $110 \text{ }^\circ\text{C}$ for 10 hours (xerogel). The other was dried under supercritical ethanol ($270 \text{ }^\circ\text{C}$, 8.0 Ma) for one hour (aerogel). After drying, as-prepared aerogel was anatase but xerogel was amorphous. The rutile phase in aerogel was observed after calcination at $800 \text{ }^\circ\text{C}$ while that in xerogel appeared at $1000 \text{ }^\circ\text{C}$. When the calcination temperature was increased from 270 to $800 \text{ }^\circ\text{C}$, the surface area of TiO_2 xerogel reduced dramatically while the calcination temperature had little effect on surface area of TiO_2 aerogel. The weight loss of aerogel was a result of carbonaceous residue. TiO_2 aerogel, which was calcined at $800 \text{ }^\circ\text{C}$, showed the highest photocatalytic activity in a degradation of reactive brilliant red X-3B. The

photocatalytic activities depended on a degree of crystallization and the level of carbonaceous residues.

Kim and Kwak [2007] prepared spherical mesoporous TiO₂ by a sol-gel method. Hydrothermal treatment was performed to increase the crystallinity, thermal stability, surface area, and photocatalytic activity of the mesoporous TiO₂. The hydrothermally treated mesoporous TiO₂ materials possessed a high crystallinity with a nanocrystalline anatase structure even in the as-synthesized state, whereas untreated materials had an amorphous or semicrystalline phase prior to calcination at 300 °C. The surface area of hydrothermally treated mesoporous TiO₂ exceeded 395 m² g⁻¹, whereas the area of the untreated materials was less than 123 m² g⁻¹. The pore size distributions of the hydrothermally treated mesoporous TiO₂ materials were narrower than those of untreated materials. The average pore size increased from 5.7 to 10.1 nm as the calcination temperature increased. The photocatalytic activity of hydrothermally treated mesoporous TiO₂ was significantly higher than the activities of untreated materials. The maximum decomposition rate was three times faster than that of a commercial TiO₂, P25. The high photocatalytic activity of mesoporous TiO₂ is due to the large surface area and high crystallinity with a nanocrystalline anatase that was induced by the hydrothermal treatment.

Venkatachalam et al [2007] varied reaction parameters such as hydrolysis agent, molar ratio, and calcination temperature during the synthesis of TiO₂ by a sol-gel method. An increase in the calcination temperature from 300 to 600 °C caused the peak intensity of anatase ($2\theta=25.3^\circ$) to become taller and narrower, suggesting an increase in crystallinity. The rutile phase started appearing at 500 °C. When TiO₂ was calcined at 800 °C, the pattern exhibited a complete rutile TiO₂ structure, indicating complete phase transformation from anatase to rutile at this temperature. The increase in the calcination temperature forced a condensation of free hydroxyl groups on the surface of TiO₂ particles. Specific surface area and pore volume decreased as the calcination temperature increased. Meanwhile, the pore diameter increased because the crystallite size of TiO₂ increased. The photocatalytic degradation of the model pollutant, BPA, over nanosize TiO₂ revealed higher activity than bulk TiO₂ (Degussa P-25). The enhanced adsorption of BPA over nano TiO₂ surface possessing high

surface area and small particle size was suggested to be the cause for higher activity of TiO_2 .

Wetchakun and Phanichphant [2008] synthesized titanium dioxide nanoparticles by hydrolysis and condensation of titanium tetraisopropoxide in absolute ethanol using cellophane membrane. The obtained powder was calcined for three hours at a temperature between 400 and 900 °C. Anatase to rutile transformation occurred at a temperature between 700 °C and 800 °C. The anatase phase composition decreased linearly from 99 wt% to 90 wt% with an increased in calcination temperature. The small rutile phase content increased from 0.15 to 0.28 wt% when the temperature was raised from 400 to 700 °C. TiO_2 calcined at 400 °C for three hours possessed the highest specific surface area of 121 m^2/g and the surface area rapidly decreased to 17 m^2/g when the calcination temperature was increased to 600 °C. The photocatalytic activities of TiO_2 nanoparticles were investigated with oxalic acid, formic acid, and malonic acid. Under near-UV irradiation, TiO_2 nanoparticles calcined at 400 °C for three hours showed the highest activity for mineralizing oxalic acid due to high specific surface area.