

CHAPTER I

INTRODUCTION

Titanium dioxide (TiO_2 or titania) has been known to be an excellent catalyst support in industrial process, (Matsuda and Kato, 1983; Inomata *et al.*, 1980; Luck, 1991) e.g., as a support in a commercial vanadium (V) oxide catalyst for selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia. Due to stricter regulations, a higher level of removal of NO_x is now required and one of the most effective approaches to meet the new goals is to use a TiO_2 support having a larger surface area. Generally, large surface areas are required for catalyst. Since the catalyst is usually used at high temperature, high thermal stability, as well as large surface area, is also important (Kominami *et al.*, 1999).

Titania is commercially very important as a white pigment because of its maximum light scattering with virtually no absorption and because it is non toxic, chemically inert, and a dielectric ceramic material for its higher dielectric constant (Cheng *et al.*, 1995). Recently, it has been suggested that monodisperse oxide powders are preferable to ceramic raw materials (Ogihara *et al.*, 1991). Titania is known to have several natural polymorphs: Rutile is thermodynamically stable which tends to be more stable at high temperatures and thus is sometimes found in igneous rocks, but anatase is metastable at high temperatures (both belonging to the tetragonal crystal system), and brookite is formed only under hydrothermal conditions or usually found only in minerals and has a structure belonging to the orthorhombic crystal system (Keesmann, 1966). Anatase type titania has been used as a catalyst for photodecomposition and solar energy conversion, because of its high photoactivity (Lason and Falconer, 1994; Kamat and Dimitrijevic, 1990; Herrmann *et al.*, 1997; Fox and Dulay, 1993; Fujishima *et al.*, 1999). On the other hand, rutile-type titania has been used for white pigment materials, because of its good scattering effect, which protects materials from ultraviolet light. Anatase titania has been reported to be unstable at high temperature and its transformation temperatures to be scattered in a wide range (Zzandena *et al.*, 1958; Yoganarasimhan and Rao, 1962). Polymorphic transformation of ceramic materials generally depends on the grain size, impurities, composition, nature of the dopant, amount of dopant, and processing (Hirano *et al.*, 2002).

Titanium dioxide (TiO₂) has been studied extensively as a photocatalyst. Application of photocatalytic reactions, such as the removal of ethylene (C₂H₄, a plant hormone that promotes the ripening of fruits and vegetables and accelerates the aging of flowers) on titanium dioxide-based materials (Park *et al.*, 1999), the effects water splitting (Fujishima *et al.*, 1972; Sato *et al.*, 1980; Kudo *et al.*, 1987; Tabata *et al.*, 1995; Kominami *et al.*, 2001), mineralization of organic compounds in water (Loddo *et al.*, 1999), organic syntheses (Nishimoto *et al.*, 2001) and reductive fixation of carbon dioxide (Ishitani *et al.*, 1993; Fujiwara *et al.*, 1997) are of great importance for both fundamental studies and practical applications. Among the various photocatalysts, titanium dioxide (TiO₂) is one of the most popular and promising materials because it is stable in various solvents under photoirradiation, it is available commercially, and it can induce various types of redox reactions. (Seoibe *et al.*, 1989; Schiavello, 1997).

Particle size is an important parameter for catalysis in general since it directly impacts the specific surface area of a catalyst with a smaller particle size, the number of active surface sites increases, and so does the surface charge carrier transfer rate in photocatalytic. However, previous study revealed that the photocatalytic efficiency does not monotonically increase with decreasing particle size, and there exists an optimal particle size of about 10 nm for pure nanocrystalline TiO₂ photocatalyst in the liquid-phase decomposition of chloroform (Wang *et al.*, 1997). This phenomenon is attributed to the increased surface e⁻/h⁺ recombination rate, which offsets the benefits from the ultrahigh surface area of nanocrystalline TiO₂.

There always exist structural defects on the surface and inside the titania particles (Torimoto *et al.*, 1996). These structural defects are related with the destiny of photoexcited electrons. Surface defects are good for high photoactivity because they are used as an active site on which the electron donor or acceptor is adsorbed. However, the bulk defect lowers the photoactivity because they provide sites for the recombination of the photogenerated electrons. According to electron spin resonance (EPR) spectroscopic study, the photoexcited electron trap at surface Ti³⁺ sites or Ti⁴⁺ sites within the bulk and holes trap at lattice oxygen ions (Howe *et al.*, 1985; Howe *et al.*, 1987; Nakaoka *et al.*, 1997). Therefore, the bulk defect should be reduced to get high photoactivity. In general, the reduction of bulk defects is achieved by high temperature calcination. Unfortunately, the anatase phase is metastable and transformed to rutile one when the calcinations temperature is over about 773 K

(Campbell *et al.*, 1992). In addition, the surface area is reduced dramatically during the high temperature calcinations. Considering the effect of bulk defects or the result of Fotou *et al.* (1996) and Ohtani *et al.* (1997), it is expected that titania particles calcined at higher temperature without transforming anatase phase to rutile phase could show a higher photoactivity.

Nanocrystalline material and nano composites characterized by an ultra fine grain size (< 50 nm). Nanocluster are subject of current interest because of their unusual magnetic, optical, electronic properties, which often difference from their bulk properties. Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NO_x , CO, CO_2 , CH_4 and aromatic hydrocarbon) with enhances sensitivity and selectivity. Nanosize metallic powders have been used for the production of gas tight materials, dense parts and porous coating (Ahmed, 1999). Nanometer-size particles have different physical and chemical properties from bulk materials. When used as catalysts, their catalytic activity is expected to be enhanced not only because of their increased surface area, but also because of the change of surface properties such as surface defect (Popielarski, 1998).

The particle size of nanocrystalline titanium (IV) oxide plays an import role in the physical and chemical behavior of the material because the specific surface area, the chemical stability, and the chemical reactivity of the material are all highly correlated with particle size. It has been shown that the adsorption of organics onto surface of nanocrystalline anatase is size-dependent and that the particle size is a crucial factor in photocatalytic decomposition of chloroform by nanocrystalline anatase titania (Zhang *et al.*, 2001).

Nano-sized TiO_2 have been prepared by several methods such as solvothermal method, hydrothermal method, thermal decomposition, vapor-phase hydrolysis laser-induced decomposition, sol-gel method, chemical vapor decomposition method (CVD) and molten salt method. Wet chemical routes (sol-gel, precipitation) seem to be more efficient in controlling the morphology and degree of agglomeration of nanocrystalline particles the dry methods such as chemical vapor deposition (CVD). However, in the former methods, strong agglomerates can be easily formed among nanoparticles, because of their large specific surface area, which may lead to a degradation of properties. Titanium alkoxide and titanium chloride are usually used as precursors for TiO_2 (Bradley *et al.*, 1978). The precipitation of hard agglomerates

often occurs during hydrolysis, because these reagent exhibit high reactivity with water (Yang *et al.*, 2001).

The sol-gel method, is one of the precipitation methods, affords titanias with extremely high surface area (Zaharescu *et al.*, 1997; Dagan and Tomkiewicz, 1994). The method basically consists of the hydrolysis of an alkoxide to form a sol, followed by gelling, ageing, drying and thermal stabilization. Each step can be controlled and modified in order to obtain specific material, narrow pore size distribution, and narrow particle size distribution (Montoya *et al.*, 1992). However, the thus-obtained titanias contained some amounts of the amorphous phase and their surface area decrease drastically in calcination to improve the crystallinity (Iwamoto *et al.*, 2001), moreover, several aqueous-based methods using metal salts as a precursor material, such as the hydrolysis method and homogenous precipitation method have several problem; the concentration of reaction species should be low and the reaction time very long (Moon *et al.*, 1995).

Hydrothermal Methods have been widely applied for the synthesis of a variety of ceramic materials, while syntheses of metal oxides in organic solvents at temperature high than their boiling points (Solvothelmal synthesis) have been experiment by only a few research groups (Bibby *et al.*, 1985; Cruickshack *et al.*, 1985; Inoue *et al.*, 1991; Kominami *et al.*, 1999). Inoue *et al.* (1991) used organic media in place of water for hydrothermal method. They have explored the synthesis of inorganic materials in glycol at temperature higher than boiling point of the glycol; they call "Glycothermal Method". By solvothelmal method, nanocrystalline titanium (IV) oxide produced but mechanism of reaction occurred in several ways. At high temperature above supersaturation point, metal oxide was crystallized or precipitated which product was different in properties, morphology, crystalline etc.

In previous, synthesized titania used many solvent for preparation by the solvothelmal method (Hydrothermal and Glycothermal method). But some work interested in effect in solvent used to synthesis. In addition, the effect of metal doped on titania synthesized in several solvent is less reported.

Fischer-Tropsch synthesis (FTS) has a lively history of more than 80 years. Its name came from the work of Fisher and Tropsch and first decribed in the 1920s. It is known as a carbon monoxide (CO) hydrogenation which is added hydrogen to carbon monoxide. In general, the process is most widely used for synthesis of hydrocarbon waxes which are further cracked into gasoline and diesel fuel. The common FTS

catalysts are based on iron (Fe), ruthenium (Ru), or cobalt (Co) as the active metal. The costs for Fe-based catalysts are low, but these catalysts suffer from a low wax selectivity, deactivation, and inhibition of the productivity by water at large syngas conversions. Despite the high activity of Ru-based catalysts, their utilization is limited to scientific studies because of the high price of ruthenium. However, Co-based catalysts are preferred due to their high activity for FTS based on natural gas, high selectivity to linear hydrocarbon and low activity for the competitive water-gas shift reaction (WGS). For Co catalysts, it is known that the reduced metal, rather than its oxides or carbides, is the most active phase in CO hydrogenation. However, under pretreatment and/or reaction conditions, the formation of Co and the support results in a lower activity of the catalysts due to a loss in active Co metal available for reaction.

Support effects in FTS catalysts have been investigated. One important focus in the development of this process is the improvement of the catalyst activity by increasing the number of active Co metal sites that are stable under reaction conditions. Therefore, it is important to understand how the structural parameters of the catalyst influence the activity and stability of catalysts. To improve the number of active sites, the Co is most often present as dispersed clusters on a high surface area support such as Al_2O_3 , TiO_2 , SiO_2 , and ZrO_2 . Titania or TiO_2 is one of the most supports used for Co catalysts (Reuel and Bartholomew, 1984; Kraum and Baerns, 1999; Lin *et al.*, 2002; Jacobs *et al.*, 2002; Madikizela and Coville, 2002). However, it should be noted that titania itself has different crystalline phase such as anatase and rutile phase. The different crystalline phase composition of titania could play an important role on the catalytic performance of titania-supported Co catalysts (Jongsomjit *et al.*, 2005).

Moreover, to increase titania-supported cobalt catalyst activity, titania can be added in small amounts or mixed with some other oxides so as to improve surface characteristics (surface area and porosity), thermal stability and surface acidity of the composite catalysts and consequently their catalytic performances (Xingtao Gao and Israel E. Wachs, 1999; Mohamed Mokhtar Mohamed *et al.*, 2002; M.S. Rana *et al.*, 2003) and can be added many promoters such as Ru, Pt, Pd, B, Mn, Fe, Zn and Zr (E. IGLESIA *et al.*, 1994; D. Schanke *et al.*, 1995; JG. Price *et al.*, 1997; JL. Li *et al.*, 2000; N. Tsubaki *et al.*, 2001; NN. Madikizela *et al.*, 2002; DJ. Duvenhage *et al.*, 2002; JL. Li *et al.*, 2003; FM. Cano *et al.*, 2004; K. Nagaoka *et al.*, 2004; N. Nobuntu *et al.*, 2004). The use of these promoters as described above tends to lower the reduction

temperature of Co, preserve the activity by preventing the formation of coke, increase the reducibility of Co, increase FT reaction rates, exhibit cluster and ligand effects, act as a source of hydrogen spillover, and enhances the dispersion.

This thesis focuses on investigation of characteristics and catalytic properties for crystallite size of titania, titanium (IV) buoxide and toluene, were used to prepare nanophase titania particles by the solvothermal method and to investigate the effect of the crystallite sizes and defects density on the decomposition of ethylene. In addition, the effect of heating time on crystallite size of titania synthesized in several solvent is reported.

Objective of the thesis

1. Study of the effect of crystallite sizes on synthesized titanium dioxide by the solvothermal method on photocatalytic decomposition of ethylene.
2. Study of effect of various cobalt dispersion on crystallite size of titanium (IV) oxide.

The present study is arranged as follows:

Chapter II presents literature reviews of the previous works related to this research.

Chapter III explains the basic theory about titania such as the general properties of titania, the various preparation methods to obtain the ultrafine titania and basic theory about photocatalytic reaction.

Chapter IV shows the experimental equipment and systems, and the preparation method of titania by solvothermal method.

Chapter V exhibits the experimental results.

In the last chapter, the overall conclusions and recommendation for the future studies of this research are given.

Finally, the samples of calculation for the preparation of titania and crystallite size are included in appendices at the end of this thesis.