CHAPTER I

INTRODUCTION

In the last decade the hydrothermal processing has been widely used for the preparation of crystalline metal oxides as an alternate or new approach because it is essentially less energy intensive, less polluting and leads to high homogeneity and well-crystallized (Diamandescu et al., 1999). There has been interested to study the thermal reactions to synthesis metal oxide using organic media instead of water such as glycol (glycothermal reaction) and demonstrated that various novel and characteristic crystalline products were obtained directly by these reaction. Metal oxide materials prepared by this method are high surface area and high porosity materials that are attractive in applications such as insulators, ceramic precursors and catalyst support (Clapsaddle et al., 2003).

Titanium (IV) oxide has been known to be an excellent catalyst support in industrial process e.g., as a support in a commercial vanadium (V) oxide catalyst for selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia (Kominami et al., 1995) and the selective oxidation of hydrocarbon and as photocatalysts for various reactions. Besides catalytic applications, it also has many uses such as pigment, filler, more recently, membrane and anti-reflection coating (Iwamoto et al., 2000).

There are seven known polymorphs of titania, six of which have distinct structures (Banfield et al., 1991). Three of these polymorphs, rutile, anatase, and brookite occur in nature. Rutile is thermodynamically stable which tends to be more stable at high temperature 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, 1996). Anatase type titania has been used as a catalyst for photodecomposition and solar energy conversion, because of its high photoactivity. On the other hand, rutile-type titania has been use 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 temperature to be scattered in a wide range. 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).

The particle size of nanocrystalline titanium (IV) oxide plays an important 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 on to 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., 2000).

Surface area is one of the important factors for the use of titania as catalyst materials. However, large-surface area materials have high tendency for sintering because of their surface energies. Amorphous titania having extremly large surface area has been prepared by sol-gel method (Zaharescu and Crisan, 1997; Dagan and Tomkiewicz, 1994 ; Montoya et al., 1992) ; however it crystallizes into anatase at around 500°C, which is accompanied by marked decrease in surface area.

Since thermal stability seriously affects the catalyst life, titania having large-surface area with resonable thermal stability has been sought. Thus many studied have been devoted to improve the thermal stability of titania using additives such as Al, Si, La, and others. The effects of these additives are quite different by the procedures of the doping and amounts of the additives, and the mechanisms for the stabilization effects of these dopants are not yet elucidated (Iwanoto et al., 2000).

Nanosized large-surface-area titania powders have been prepared by several methods such as hydrothermal method, solvothermal method, sol-gel method, thermal decomposition of alkoxides, vapor-hase hydrolysis laser-induced decomposition, chemical vapor decomposition method (CVD), and molten salts method. Some of these products were found to show a relatively high thermal stability even after calcination at 500-600°C. Wet chemical routes (sol-gel, precipitation) seem to be more efficient in controlling the morphology and degree of agglomeration of nanocrystalline particles. 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 occur 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 Tomikiewicz, 1994). The method basically consists of the hydrolysis of an alkoxide to form a sol, followed by gelling, aging, 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 synthesis of metal oxides in organic solvents at temperature higher than their boiling points (Solvothermal synthesis) have been experimented by only a few research groups (Bibby et al., 1985; Cruickshack et al., 1985; Fanelli et al., 1989; 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 glycols at temperature higher than boiling point of the glycol, they call "Glycothermal Method". By solvothermal 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 products was different in properties, morphology, crystalline etc.

Hematite, α-Fe_2O_3 nanocrystals have shown several excellent properties and found a wide field of technological applications including fabrication of ferrites, catalysis, inorganic pigments, raw material for magnetic recording media, colour imaging, magnetic memories for computer, magneto-optical devices, magnetic refrigerators and sensors. The preparation method determine the final powder characteristics like shape, average particle size, specific surface porosity, that are of considerable importance in the subsequent processing for specific applications (Diamandescu et al., 1999).

Several synthetic methods have been developed for preparation of hematite nanocrystals including sol-gel, hydrolysis of iron salts and hydrothermal synthesis. (Reddy et al., 2000; Sesigur et al., 1996; Suber et al., 1999). The magnetic nanocrystals prepared by sol-gel method are high surface area and high porosity. The versatility of sol-gel chemistry provides a means of controlling the shape, morphology and texture properties of the final materials (Brinker and Dcherer, 1989). Sol-gel method also provides a means of preparing mixed metal oxides in which mixing of two or more metal oxides phases can be controlled on both the molecular-and the nanoscale.

Hydrothermal synthesis has shown to be advantageous over other methods in homogeneous nucleation and grain growth of hematite nanocrystals. Preparation conditions such as concentration, reaction temperature and time are the main factors in determining the morphologies and structures of nanocrystals prepared by hydrothermal conditions. For example, hydrothermal reactions of an aqueous iron nitrate solution at a wide concentration range produce porous hematite nanocrystals (40-80 nm) containing non-intersecting 5-20 nm pores, while lowering the concentration to 0.0027-0.18 M yields some amounts of a second phase that is mainly α-FeOOH (goethite). Single phase α-Fe_2O_3 (hematite) can be formed in ferric chloride hydrothermal systems. However, the ferric concentration has to be restricted as low as 0.02-0.04 M. Beyond this range, second phase β-FeOOH can be readily formed. It is clear that hematite nanocrystals can be obtained by adjusting hydrothermal conditions, but nanocrystals formed in this manner tend to agglomerate.

Zinc oxide (ZnO) has been used in various technologies including use in medicines (ointments), gas-sensor, catalyst, pigment, semi conductors, and as the main component in varistors, which are used in surge suppressors for circuit overvoltage protection. These various applications of ZnO are due to the specific chemical, surface and microstructural properties of ZnO. The microstructural and physical properties of ZnO can be modified by introducing changes into the procedure of its chemical synthesis.

ZnO-based ceramics are characterized by high nonlinear current-voltage properties, and this effect was utilized in varistors, i.e., devices for protection against abrupt increase of the voltage. In the varistor applications the microstructural properties of ZnO are the most important factor. The best varistor quality can be achieved by a high homogeneity of the packed particles which exhibit nonlinear current-voltage properties at their boundaries. On the other hand, for the application of ZnO as humidity sensor, the opposite properties of ZnO are required and in this case, the material must possess a very open, porous microstructure with a controlled pore size. The sensitivity and response times of ZnO-based humidity sensors strongly depend on the porosity of this material. In the catalytic applications of ZnO the surface acid/base properties and the adsorption capacity are the most important functional parameters. For the application of ZnO as pigment, the morphology and particle size are essential parameters.

ZnO particle morphologies are very complex and diversiform in comparison with that of TiO_2. So far, monodispersed ZnO particles with well-defined morphological characteristics, such as spherical, ellipsoidal, needle, prismatic, and rod-like shapes have been obtained. Aggregates composed of these basic shape particles have also been achieved (Li et al., 2003). Various technique have been employed for the preparation of

ZnO nanoparticles, which include sol-gel, physical evaporation, pulsed laser ablation, flame pyrolysis and hydrothermal synthesis.

As a method for preparing high-quality ceramic powders, the hydrothermal synthetic route has advantages to obtain high crystallized powders with narrow grain size-distribution and high purity without treatment at high temperature. The particle properties such as morphology and size can be controlled via the hydrothermal process by adjusting the reaction temperature, time and additives (Matijevic and Ceram, 1998; Adair et al., 1998).

In previous, synthesized titanium (IV) oxide, iron (III) oxide and zinc (II) oxide used many solvent for preparation by the solvothermal method (Hydrothermal and Glycothermal method). But some work interested in the effect of solvent used to synthesis. In addition, the effect of metal doped on these metal oxides synthesized in several solvents is less reported. In this work, the study will focus on the effect of solvent, synthesis temperature and silicon on size and thermal stability of titanium (IV) oxide, iron (III) oxide and zinc (II) oxide. After that, the physical properties of titania, iron (III) oxide and zinc (II) oxide are analyzed such as surface area, crystallite size, thermal stability and compared the properties of the product synthesized in the different solvents.

Objective of the thesis

1. To study the effect of solvent and reaction temperature on the crystallite size of titanium (IV) oxide, iron (III) oxide and zinc (II) oxide.

2. To study the effect of silicon on crystallite size and thermal stability of titanium (IV) oxide, iron (III) oxide and zinc (II) 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 titanium (IV) oxide, iron (III) oxide and zinc (II) oxide such as the general properties and the various preparation methods to obtain these metal oxides

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

Chapter V exhibits the experimental results.

In the last chapter, the overall conclusion of this research are given.

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