CHAPTER I
INTRODUCTION

The preparation of titanium (IV) oxide (TiO_2, titania) is the subject of considerable interest because this material is widely used as catalyst supports for the selective catalytic reduction (SCR) of NOx with ammonia and the selective oxidation of hydrocarbon, and as photocatalysts for various reactions. Besides catalytic applications, it also has many uses such as pigment, filter, more recently, membrane and anti-refection coating.

Surface area is one of the important factors for the use of titanium (IV) oxide as catalyst supports. Generally, large-surface areas are required for catalyst supports to disperse a catalyst material effectively and to increase the number of active site in the catalyst. However, large-surface area materials have high tendency for sintering because of their surface energies. Amorphous titanium (IV) oxide having extremely large-surface area has been prepared by sol-gel method; however it crystallizes into anatase around 500 °C, which is accompanied by a marked decrease in surface area.

Since thermal stability seriously affects the catalyst life, titanium (IV) oxide having large-surface area with reasonable thermal stability has been sought. Thus, many studies have been devoted to improve the thermal stability of titanium (IV) oxide 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 full elucidated. One possible method for the preparation of thermally stable titanium (IV) oxide seems to be direct synthesis of well–crystallized materials.

Titanium (IV) oxide for catalytic applications is usually prepared from titanium oxysulfate ($TiO(SO_4)$), sulfate ($TiO(SO_4)_2$), or chloride ($TiCl_4$) by the precipitation (or hydrolysis) method. However it is known that the counter anion of the starting titanium salt remains in the product and effect the activity of the catalyst.

To avoid the contamination of the counter anion, titanium alkoxide can be used as the starting material for catalysts, catalyst supports, and photocatalysts.

In most of the synthetic processes, the alkoxides are hydrolyzed in an alcoholic solution yielding amorphous (or hydrated) metal oxide with large-surface areas; however their surface areas are drastically decreased on calcination at the temperatures where corresponding oxide begin to crystallize. Recently, Inoue et al. have examined the thermal reaction of metal alkoxide in glycols (glycothermal reaction) or other organic media and demonstrated that a number of novel or characteristic crystalline products can be obtained directly without bothersome procedures such as purification of the reactants or handling in inert atmosphere.

By applying this method, nanocrystalline anatase having large-surface area (> 50 $m^2 g^{-1}$ after calcination at 550°C) were obtained by the reaction of $TiO(acac)_2$ in toluene. Further optimization of the reaction conditions and careful choice of the titanium source and organic solvent provided anatase nanocrystals having an extremely large-surface area (> 100 $m^2 g^{-1}$ after calcination at 550°C). However, transformation of anatase into rutile took place in the temperature range of 600 - 1000 °C resulting in drastic decrease in surface area. To improve the thermal stability of titanium (IV) oxide, the silica-modified titanium (IV) oxides were prepared by the glycothermal method and have found that these materials had quite large-surface area and exhibited high thermal stability.

As mentioned above, the novel method for the synthesis of metal oxides in organic media may be a new route to prepare micro- and nanocrystalline metal oxides. Physical properties of the product can be controlled by the choice of the organic solvent, reaction conditions, and strengthen of the alkyl group of the metal alkoxides. In this study, the novel method was applied in the system silica modified titanium (IV) oxide and focus on:

1.The effect of amounts of tetraethyl orthosilicate (TEOS, silica content) on the physical properties and thermal stability of nanosized titanium (IV) oxide samples

2.The effect of the reaction of crystallite formation (type of organic solvent) on the physical properties and thermal stability of nanosized titanium (IV) oxide samples.

The present study is arranged as followed:

Chapter II presents a literature reviews of the novel synthesis of several metal oxides and binary metal oxides in organic media.

The theory related to this work, physical and chemical properties of titanium (IV) oxide, preparation processes, titanium (IV) oxide uses and others are described in chapter III.

Chapter IV presents the experimental systems and the catalyst preparation.

Chapter V shows the experimental results of the characterization of catalyst samples .The X –Ray Diffraction (XRD) patterns, BET surface area, morphology and FT-IR absorption spectra are explained.

In the last chapter, the overall conclusion emerged from this research is given.

Finally, the sample of calculation of catalyst preparation, BET surface area and crystallite size are included in APPENDICES at the end of this thesis.