CHAPTER I

INTRODUCTION

It has been known that defect structure is the main factor influencing the properties of crystalline material (especially at the nanoscale level). However, studying in field of defect structure is difficult because there are many types of defect structure. Based on theory, defects are either Frenkel and or Schottky defect. These types do not cover all the types of defect found in real materials. Although, the defect structure is an important factor in field of material, there are few research groups which study in the field of defect controlling and its application. Therefore, we engage to study the defect controlling and its application on a simple nanocrystal material such as TiO_2.

It has been known that TiO_2 is a material of great interest. It is well-known for its applications in the field of photocatalytic reactions [1-6], catalyst support [7-8], and as sensors. TiO_2 always possesses structural defects on the surface and inside the TiO_2 particles [9]. Although, the bulk defect is important factor to control in order to improve the level of perfection of the crystal, the surface defect is more important than the bulk structure for applications of surface science such as catalysts and support.

The defect structure of TiO_2 in bulk is difficult to control and detect (it can be detected only by the Rietveld analysis from XRD). However, there are few reports which discussed this topic such as Jung et al. [10], Wang et al. [11-12]. They concluded that bulk defect detected by the Rietveld analysis decreased with increasing annealing temperature. Moreover, these bulk defects increased with increasing the amount of metal doping. In case of surface defect, there are a few types of surface defect. However, Henrich and Kurtz have shown that the dominant defects on TiO_2 surfaces are oxygen vacancies (Ti^{3+}) [13]. There are many studies of this topic because oxygen vacancies are easily detected using various techniques. Also, techniques including X-ray photoelectron spectroscopy (XPS) [14], surface vertical orbital (SVO) method [16], electron spin resonance (ESR) [17] can monitor the surface defect (Ti^{3+}) of TiO_2. However, there are only a few methods used for controlling surface defect. Some of the common methods used to create defect sites (Ti^{3+}) on the TiO_2 surface are UV radiation [19], annealing in vacuum [20], ion sputtering [20], plasma-treating [21]. These methods are the second step with the crystalline TiO_2 powder/film prepared in the first step and then the defect created in the second step. Therefore, the surface defect (Ti^{3+}) creation in the first step is a new class of defect creation and this is the goal of this work.

TiO_2 nanocrystals are usually prepared by sol-gel [23-24], gas-synthesis [25], or solvolthermal processes [26]. In the case of the sol-gel method, there are a bunch of process parameters during the preparation process that are used to control the properties of the final product such as water:precursor ratio, amount of doping, and calcination atmosphere. Therefore, in case of surface defect controlling in the new class of creation (created in first step), process parameters were controlled during sol-gel synthesis in order to affect the surface defect created in the first step. The calcination atmosphere and the water:precursor ratio were the first variables studied in this work.

There are many works reporting that the surface defect can control the properties of TiO_2 nanocrystal, therefore, in this work the effect of surface defect on the properties of TiO_2 nanocrystal and its application were investigated as the other main goal. In this work, the effects of surface defect were studied in the catalytic field as a photocatalyst for ethylene photooxidation and as a support for cobalt using in the CO-hydrogenation.

In case of thermal stability of TiO_2 nanocrystal, Depero et al. [27] and other researchers [28,29] reported that surface defect (Ti^{3+}) of the TiO_2 was the main factor promoting the crystal growth rate during high temperature. In this work, the role of surface defect on the thermal stability of TiO_2 was also investigated coinciding with the impact of initial crystallite size of TiO_2 which is also the main parameter controlling the crystal growth rate. Moreover, to understand the nature and behavior of surface defect on the surface of TiO_2 nanocrystal, the probing surface defect on TiO_2 was also studied.

This dissertation was divided to twelve chapters. Chapter I involved an overview of the importance of surface defect and also its application. In chapter II, knowledge and open literature dealing with surface defect was presented. The literature review as accentuated the technique of surface defect creation, the probing of surface defect by the common gases, the report concerning the effect of surface defect on crystal growth rate, and the applications of surface defect such as photocatalysis and support. The experimental procedure as well as the instrument and technique used for characterizing the resulting TiO_2 were also described in the Chapter III.

In Chapter V, the results on the surface defect controlling in the first step coinciding with the preparation of TiO_2 in anatase phase via sol-gel synthesis were reported. In this chapter, the surface defect was controlled by varying the calcination atmosphere. The surface defect controlling by varying the water:alkoxide molar ratio was also reported in Chapter VI. The main mechanisms explaining the formation of surface defect were also mentioned together with the comparison between the surface defect controlling technique studied in this work and the other techniques.

In Chapter VII, the role of surface defect in TiO_2 nanocrystal on the photoactivity decomposing the ethylene was investigated. The mechanism as a self promotion of surface defect was proposed based on the literatures and our results.

In Chapter VIII, the impact of surface defect in TiO_2 support on the characteristics and catalytic properties of cobalt for the CO-hydrogenation were investigated as the main goal. The influence of surface defect on the metal support interaction was mentioned explaining the role of surface defect on the cobalt catalyst. The effects of surface defect and perfect sites on the formation of Co-SCF which is a non-reducible compound were also mentioned in the Chapter IX.

In Chapter X, the role of surface defect in TiO_2 nanocrystal preparing from various preparation method on the thermal stability was reported here. Using the Piyasan's equation dealing the growing of nanocrystal at high temperatures (which is explained as the function of initial crystallite size), the impact of surface defect coinciding with the impact of initial crystallite on the thermal stability of TiO_2 were investigated in this chapter.

In Chapter XI, the probing of surface defect by using the metal carbonyl and characterizing via the EXAFS technique was reported here. The consistency between ESR and IR technique interpreting the surface behaviors of surface defect and hydroxyl group were used for making a surface model. The characterization in the atom level by using EXAFS was also used for understanding the nature of surface defect.

Finally, conclusions of this work and some recommendations for future research work were provided in Chapter XII.