

CHAPTER II

LITERATURE REVIEWS

TiO₂ has been studied extensively in the field of surface science due to the wide range of its applications and the expectation that insight into surface properties on the fundamental level will help to improve its properties [14]. The surface defect is one of the important topics in this field because the properties of the TiO₂ nanocrystal are often dependent on a nature and density of the surface defect sites. As known that, TiO₂ is a useful material for many applications. Therefore, several studies have addressed its applications such as photocatalytic reaction, metal-support catalyst, and also its properties such as crystal growth. The common techniques used for creating surface defect were also reported by many researchers. Moreover, several methods for probing surface defect of TiO₂ were discussed as well.

2.1 Defect (Ti³⁺) controlling on TiO₂

2.1.1 Bulk defect controlling

Defect structure of TiO₂ in bulk is difficult to control and being detected (it can detect only Rietveld analysis from XRD) because it has several types of defect. However, there are only few works which discussed in this topic such as Jung et al. [10], Wang et al. [11-12]. They concluded that bulk defect (which is detected by using Rietveld analysis) decreased with increasing annealing temperature. Moreover, these bulk defects increased with increasing the amount of metal doping.

2.1.2 Surface defect controlling

There are a few types of surface defect on TiO₂. However, Henrich and Kurtz have shown that the dominant defects on TiO₂ surfaces are only oxygen anion vacancies [13]. Some of the common methods to create defect sites on the TiO₂ surface are UV radiation [19], annealing in vacuum [20], ion sputtering [20], plasma-treating [21]. These

methods are the second step which means that the crystalline TiO_2 must be prepared in the first step and then the surface defect must be created on this crystalline TiO_2 in the second step. Therefore, the surface defect creation in the first step is the new class of creation. Based on the high photoactivity of TiO_2 in the anatase phase, Yamazaki et al. [2], Park et al. [3], reported that an increase of surface defect (Ti^{3+}) can enhance its photoactivity by the photoelectron trapping. Further, to improve the hydrophilic property, Sakai et al. [30,31,32] reported that surface defect (Ti^{3+}) on anatase is an important parameter controlling this property. Also as a support with high surface area of anatase, Wallace et al. [33] reported that surface defect (Ti^{3+}) plays the significant roles enhancing the dispersion and stability of supported gold cluster via the strong interaction (SMSI) between the defect site and metal cluster. Thus, it demonstrates that the creation of surface defect (Ti^{3+}) on anatase is necessary for improving its properties for many applications. However, nearly all of the common techniques for surface defect (Ti^{3+}) creation (the so-called the second step creation technique) prefers the rutile and it is difficult to create surface defect on the anatase. This is because the surface must be cleaned at high temperature before creation [13,18,34,35,36,37]. In addition, some second step creation techniques were carried out under high temperature caused of phase transformation and significant surface area loss [18,34,37,38,39]. Moreover, for another reason, compared to rutile, the surface of anatase shows less tendency to form oxygen vacancies, because the removal of a bridging oxygen leads to the formation of a four-fold coordinated Ti site, which is less stable than a five-fold coordinated Ti site formed at oxygen vacancies on rutile [40,41]. Therefore, the surface defect (Ti^{3+}) creation in the first step coinciding with the preparation of crystalline TiO_2 in anatase phase (the so-called the first step creation technique) should be the valuable ideals for improving the properties of TiO_2 nanocrystal.

2.2 Effect of surface defect (Ti^{3+}) on photocatalytic reaction and hydrophilic properties of TiO_2 nanocrystal.

One of the most commonly studies, and often the most effective photo-catalyst is TiO_2 , which combines the advantages of being cheap and non-toxic. In case of surface

defect, Park et al. [3] and other researchers [2] reported that if the surface defects (Ti^{3+}) are present to trap the electron, an e^-h^+ recombination can be prevented, then the subsequent reactions caused by the electrons and holes may be dramatically enhanced. However, no experimental data have proved on effect of Ti^{3+} on the photocatalytic activity so far. Moreover, to improve the hydrophilic property, Sakai et al. [30,31,32] reported that surface defect (Ti^{3+}) on anatase is an important parameter controlling this property because it can inhibit the recombination process of $e-h^+$ generated during UV irradiation. Sakai et al. also reported that the surface defect can dissociate water to be a hydroxyl group intact on the surface of TiO_2 resulting to the enhancement of hydrophilic properties of TiO_2 nanocrystal.

2.3 Effect of surface defect (Ti^{3+}) on gas-adsorption on TiO_2

Many researchers showed that surface defect and surface perfect on TiO_2 surface play significant roles as a crucial point for a gas-adsorption [15,42,43,44,45] such as adsorption of CO , CO_2 , H_2 , and H_2O . They reported that it has two distinct gases desorption peaks at different temperatures. Therefore, it was shown that the physical and chemical properties of surface defect were different from the surface perfect.

2.4 Effect of surface defect on metal-support interaction on Co/TiO_2 catalyst

The interaction between a support and a metal oxide (catalyst) precursor is an important factor used to determine the dispersion of a metal catalyst and hence the behavior of a catalyst as well [46]. In fact, the synthesis of highly dispersed cobalt catalysts requires the initial formation of very small Co_3O_4 crystallites. It was reported that the formation of small oxide clusters needs strong interactions between the support and the cobalt precursor. However, too strong interaction would suppress reduction of these CoO_x clusters [47] resulting in low reducibilities. Moreover, strong interaction between Co and TiO_2 can produce the suboxide at interface that is more resistant to reduction than the other supports. There also are many reports showing the effect of surface site as a surface defect on the interaction of metal and oxide, as summarized by

Diebold [14]. It has been known that the bond energy for anchoring of the metal is larger at the surface defect site than at the perfect sites [23]. This is because the surface defect sites have one lone pair electron at d orbital resulted in the higher reactive with the metal and oxide loading [14]. Based on this bond energy, Wallace et al. summarized the role of Ti^{3+} site on Au cluster nucleation, growth, and stability on Ti^{3+} site of TiO_2 support [33]. It showed that an increase of Ti^{3+} site strongly decreases the rate of Au cluster migration during high temperature condition due to the strongly bonding between Ti^{3+} site and Au cluster. Also the reports showing the strong bonding between Gr. VIII metals and Ti^{3+} have been done by many researchers [14,48,49].

2.5 Role of surface defect (Ti^{3+}) on the crystal growth (thermal stability) of TiO_2 nanocrystal

It has been known that the photo and chemical properties of TiO_2 are size-dependent, especially in the nano-level. However, the significant increasing of grain size can occur when the crystalline TiO_2 was placed into the high temperature surrounding. Therefore, one of the major considerations for nano-sized crystalline TiO_2 is the improving of the thermal stability. In fact, it is crucial to investigate the main parameter influencing the crystal growth rate during high temperature. Depero et al. [27] and the 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. Chen et al.⁹ also reported that the increasing of crystallite size during high temperature could be explained tentatively by surface defect as an oxygen vacancy site (Ti^{3+}) because the rate-controlling mechanism on the crystal growth of TiO_2 was the oxygen diffusion which depended on the concentration of surface defect on TiO_2 .

2.6 Probing surface defect (Ti^{3+})

Molecular probes have been investigated for understanding surface defect (Ti^{3+}) by many researchers. Rusu et al. [37] showed that the surface defect (Ti^{3+}) can be probed by using the thermal photo-desorption of O_2 . Thomson et al. [39] also reported the

probing surface defect on TiO_2 by using thermal desorption of CO_2 . The thermal desorption of CO was also used as a molecular probing the surface defect [50]. These methods distinguish surface defect from the surface perfect sites, for example. The probe molecules O_2 , CO, and CO_2 that have been used to characterize TiO_2 are weakly bound to the surface defect sites, being desorbed at temperatures well below ambient.