

CHAPTER VII

IMPACT OF SURFACE DEFECT (Ti^{3+}) PRESENT IN TiO_2 ON PHOTOACTIVITY DURING ETHYLENE PHOTOOXIDATION

TiO_2 is a material of great interest, which mainly resides in its application as pigment to give whiteness and/or opacity in paints, plastic, photocatalytic, support and paper [86]. In case of photocatalytic, titania can be used in many applications such as water cleaning and delay of ripening of fruit. Titania consists of three phases, i.e. anatase, rutile, and brookite. Many researchers reported that anatase has the highest photoactivity when compared to rutile and brookite [67,87].

In order to improve photoactivity of photocatalysts, it is necessary to understand the basic mechanism of electron-hole pair generation and its destiny. When a photocatalyst is exposed to UV irradiation with energy that is higher than band gap energy of titania, electron-hole pairs are generated and participate in the reaction as electron donors and acceptors [1].

Titania nanocrystal is usually prepared by sol-gel method [88]. It always exists structural defects on the surface and inside the titania particles [89]. Using electron spin resonance (ESR), photo generated electrons was found to be trapped at surface defect (oxygen vacancy site, Ti^{3+}) or in the bulk at Ti^{4+} sites and holes trap at lattice oxygen ions [16]. In this manner, surface defects are good for high photoactivity because they are used as an active site on which electron donor or acceptor is adsorbed. However, the bulk defect lowers the photoactivity because they provide sites for the recombination of the photogenerated electrons [84].

The use of a variety of techniques including X-ray photoelectron spectroscopy (XPS) [38], O_2 photodesorption [37], surface vertical orbital (SVO) method [15], electron spin resonance (ESR) [16] and CO_2 -temperature program reduction (TPD) [39] can monitor surface defect of titania. From CO_2 -TPD analysis, which is probe-monitored and presented surface defects of TiO_2 [39], It revealed signals between the ranges of 123 to 253 K assigning to CO_2 desorped from TiO_2 surface. As discussed,

the separated two peak (max. @ 170 and 200) indicated two structure of surface of titania. It was reported that peak at ca. 170 K was attributed to CO₂ molecules bound to regular five-coordinate Ti⁴⁺ site referred as perfected titania structure. However, the second peak at ca. 200 K was assigned to CO₂ molecules bound to Ti⁺³(oxygen vacancy site) referred as defected titania structure. ESR also showed that surface of titania has two main structures; Ti⁴⁺ and Ti³⁺ forms [16].

In the present, effects of surface defect on characteristics and photoactivities of TiO₂ were investigated and studied activity photocatalyst using oxidation of ethylene. CO₂-TPD and ESR were used as probe monitor for showing defect site on titania surface. This work proposed role of surface defect on photoactivity which this defect can be considered as self-promoter of titania photocatalyst.

The nomenclature used for the catalyst samples in this study is following:

- TiO₂(X): the calcined titania with X% of O₂ in feed during calcination.
- TiO₂(H₂): the treated titania with hydrogen in feed during calcination.

7.1 Powder X-ray diffraction

X-ray diffraction results comparing the O₂ and H₂ calcination are shown in Figure 7.1. As known that the TiO₂ resulting from O₂-calcination exhibited in the anatase phase [59]. In case of H₂-calcined TiO₂, it also exhibited in anatase phase. Based on Sherrer's equation, these samples had crystallite sizes in the range of 7-8 nm except for the TiO₂(H₂) which had crystallite size 5 nm. It can be observed that the lowest degree of crystallinity was found in TiO₂(H₂) when compared to titania samples which were calcined under oxygen atmosphere because it has high bulk defect density [61].

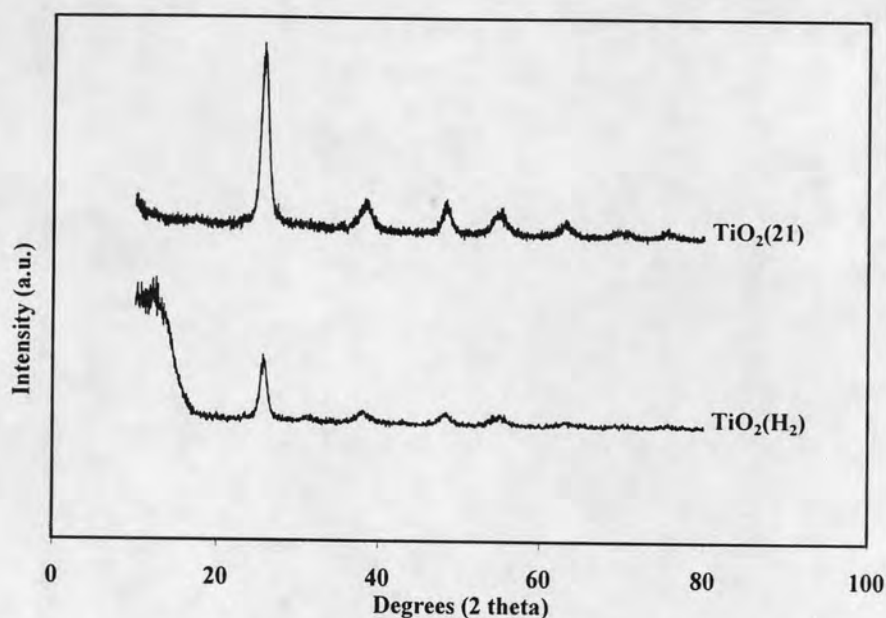


Figure 7.1: XRD patterns of TiO₂

The measured BET surface areas of titania samples that had been treated by O₂ were in the range of 98-114 m²/g (Table 5.2). In case of titania which was treated under hydrogen atmosphere [TiO₂(H₂)], it found that surface area was not significantly different from the other atmosphere (m²/g).

7.2 Scanning and transmission electron microscopy

Typical SEM micrographs of samples; (a) TiO₂(21) and (b) TiO₂(H₂) are shown in Figure 7.2. These indicate that the particles are spherical in nature. Based on SEM results (not shown all samples), all titania samples exhibited the same morphologies and particle size except for TiO₂(H₂) [Figure 7.2(b)]. It showed that TiO₂(21) has more uniform size and less agglomeration of particles as compared to TiO₂(H₂) [Figure 7.2(b)].

The TEM micrographs of samples; (a) TiO₂(21) and (b) TiO₂(H₂) are also shown in figure 7.3 which confirmed the nanoscale size particles and indicated that TiO₂(H₂) has negligible agglomeration as compared to TiO₂(21). The difference in agglomeration may result from the difference in the amount of surface hydroxyls. The surface hydroxyls of oxides were considered to be one of the main reasons for driving

the aggregation of grains due to the hydrogen bonding between these hydroxyls [90]. Therefore, this revealed that titania have more surface hydroxyl in case of oxygen atmosphere than that which was treated with hydrogen atmosphere.

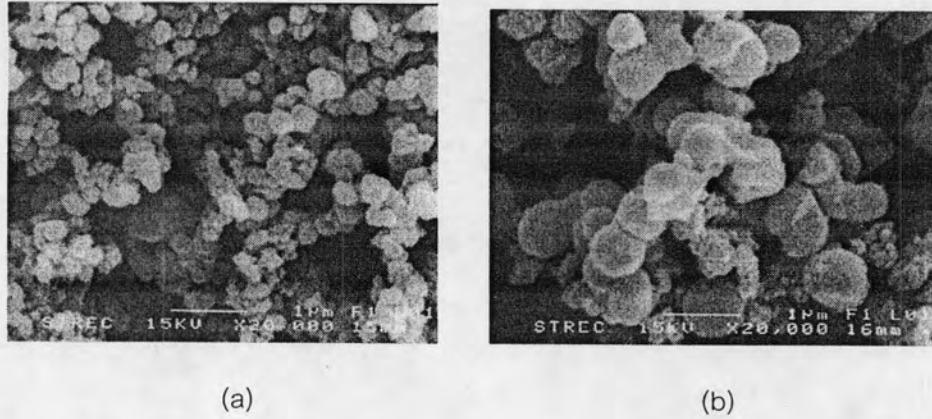


Figure 7.2: SEM micrograph of TiO₂



Figure 7.3: TEM micrograph of TiO₂

7.3 CO₂-temperature program desorption (CO₂-TPD)

Thermal desorption spectra of CO₂ from a titania surface are shown in Figure 7.4. As mentioned in the chapter 5, it revealed two desorption peaks at temperatures ca. 175 and 200 K meaning Ti⁴⁺ and Ti³⁺ sites. In case of TiO₂(H₂), the highest surface defect was observed compared with those in samples calcined with oxygen. Wu et al. [61] also reported that H₂-treated titania had high bulk defect density. It was showed that titania treated under hydrogen atmosphere had bulk and surface defect more than those calcined under oxygen atmosphere.

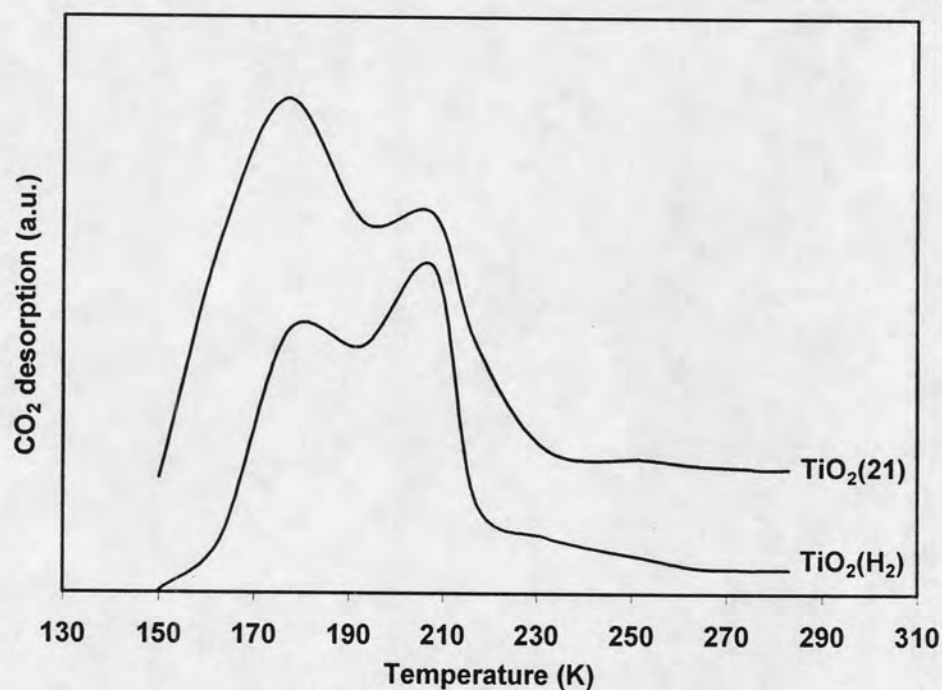


Figure 7.4: Thermal desorption spectra for CO₂ adsorbed on titania calcination at different atmosphere

3.5 Electron spins resonance spectroscopy (ESR)

Based on ESR analysis of TiO₂ as shown in the chapter 5, exhibited mainly one signal at g value of 1.996. The markedly increase in intensity of TiO₂ that had been treated by H₂ was shown in the Figure 7.5 corresponding with the result from CO₂-TPD.

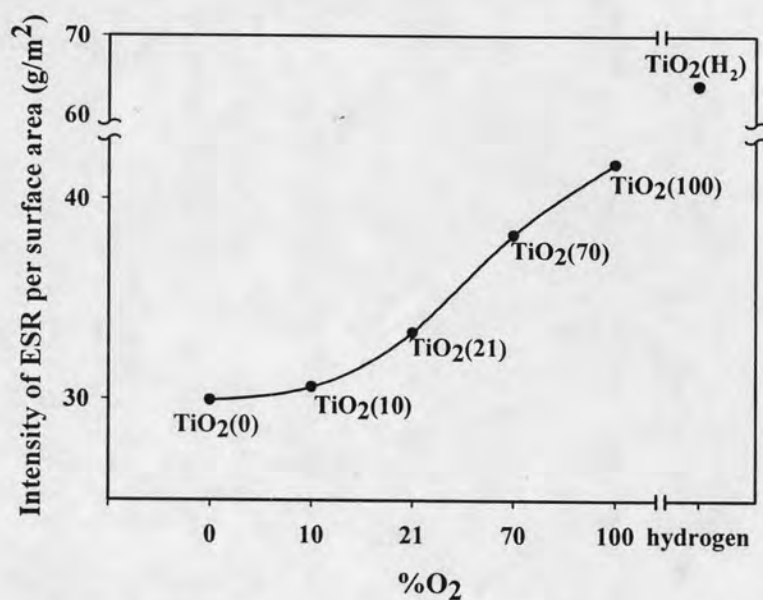


Figure 7.5: Intensity of ESR spectra per surface area of TiO₂

3.6 Photocatalytic decomposition of ethylene

Photocatalytic activity was one of the typical properties of nanocrystalline TiO₂. In our experiment, photocatalytic decomposition of ethylene was utilized to probe the surface defect. Photocatalytic properties of all titania samples are shown in Figure 7.6. From these results, it can be concluded that photoactivity of titania increased with increasing of Ti³⁺ site present in titania surface. In case of atmospheric study, it was found that surface area of titania did not control photoactivity of TiO₂, but it was the surface defect in titania surface. In case of TiO₂(H₂), it was shown that conversion of ethylene was the lowest when compared to the other titania. The CO₂-TPD showed that surface defect evidently increased, but XRD result showed that TiO₂(H₂) had the lowest crystallinity. Wu et al. [61] reported that H₂-calcined titania has high bulk defect density. It showed that TiO₂(H₂) had bulk and surface defect more than the other titania. From this result, it can be concluded that photoactivity of titania not only controlled by surface defect but also bulk defect. One of the notable characteristics of TiO₂ is that oxidizing power of the holes is greater than the reducing power of the excited electrons [1]. Although, the lattice oxygen ions are active site of this photocatalytic reaction because it is the site for trapping holes [16], this work showed that the presence of oxygen vacancy site (Ti³⁺ site) on surface titania can

enhance activity of photocatalyst too. Because oxygen vacancy can increase the life time of separated electron-hole pairs, therefore, Ti^{3+} site can be considered as self-promoter of titania photocatalyst. Simplified scheme of self-promoter was proposed in Figure 7.6. When photocatalysts is exposed to UV irradiation ($h\nu$) with energy that is higher than the band gap energy of titania, electron in valence band is excited and then it jumps to conduction band. Photogenerated electron (e^-) and holes (h^+) diffuse to the surface of titania. Photogenerated electron is trapped at Ti^{3+} site or it reduces O_2 to superoxide radical anion ($\cdot O_2^-$) directly or it can occur in trapping step first and then reduction step. In case of holes, it is trapped at lattice oxygen ions or it oxidizes adsorbed water molecules to hydroxyl radicals ($\cdot OH$) directly or it can occur in trapping step first and then oxidation step too [1]. However, when Ti^{3+} is insufficient, photogenerated electron in conduction band jumps to valence band and then it recombined with holes which this recombination process makes oxidation of adsorbed water does not occur. Therefore, when the amounts of defect sites (Ti^{3+}) at surface increases, photoactivity of the catalysts increases as well.

Table 7.1: Photocatalytic properties of TiO_2 samples.

Sample	C ₂ H ₄ conversion (%) ^a		Rate (mol/g cat.h) ^b	
	Initial ^c	SS ^d	Initial	SS
TiO ₂ (0)	41	40	75	74
TiO ₂ (10)	46	43	85	79
TiO ₂ (21)	47	48	86	88
TiO ₂ (70)	59	60	109	110
TiO ₂ (100)	62	61	114	112
TiO ₂ (H ₂)	25	25	46	46

^a Photocatalytic reaction was carried out at 40-55 °C, 1 bar, and 0.1% ethylene in air.

^b Error 5%.

^c After 5 min of reaction.

^d After 3 h of reaction.

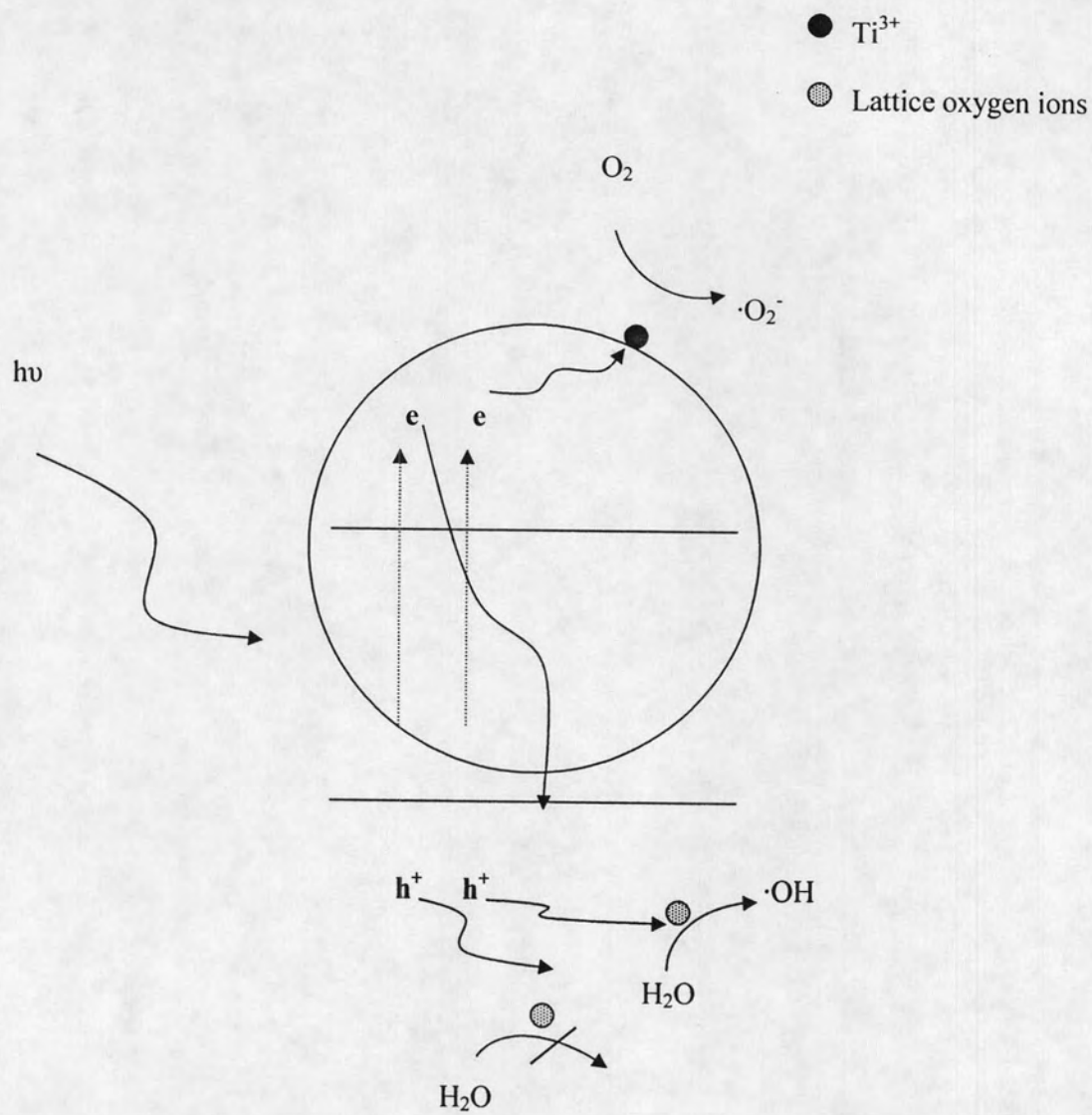


Figure 7.6: Simplified scheme of self-promoter