

## CHAPTER XII

### CONCLUSIONS AND RECOMMENDATIONS

#### 12.1 Conclusions

##### **12.1.1 Surface defect ( $Ti^{3+}$ ) controlling on $TiO_2$ nanocrystal using various calcination atmosphere as the first step for surface defect creation**

In this work, a new method for surface defect creation coinciding with crystalline  $TiO_2$  preparation in the first step was performed by changing the amounts of oxygen fed during the calcination process. Using  $CO_2$ -TPD and ESR, it was found that the surface defect density ( $Ti^{3+}$ ) could be increased by increasing the amount of oxygen fed. Also, the increased  $Ti^{3+}$  amounts did not result from the reduction of  $Ti^{4+}$  to  $Ti^{3+}$  due to low calcination temperature used in the absence of hydrogen. We propose that the removal of the surface hydroxyl group when exposed to increased oxygen concentration accounts for the formation of the surface defect ( $Ti^{3+}$ ).

##### **12.1.2 Surface defect ( $Ti^{3+}$ ) controlling on $TiO_2$ nanocrystal using various water:alkoxide molar ratio used during sol-gel synthesis as the first step for surface defect creation**

In this work, the new technique as the first step creation for creating the surface defect ( $Ti^{3+}$ ) has been developed by controlling a water:alkoxide molar ratio during sol-gel synthesis under ultrasonic irradiation. The surface defect has been successfully created at mild temperature coinciding with the preparation of crystalline  $TiO_2$  in anatase phase. No phase transformation and significant surface area loss on the resulting anatase after surface defect creation which is valuable for many application of  $TiO_2$ . Moreover, it should be mentioned that this new promising technique consumes comparatively less energy, time and special knowledge than the common techniques (the so-called the second step creation).

### **12.1.3 Impact of surface defect (Ti<sup>3+</sup>) present in TiO<sub>2</sub> on photoactivity during ethylene photooxidation**

In this work, effect of surface defect on characteristics and photoactivities of titania was investigated. From CO<sub>2</sub>-TPD analysis and ESR, the prepared titania samples in this work have two types on surface, Ti<sup>4+</sup> referred to a perfect site of titania and Ti<sup>3+</sup> referred to a defect site which comes from oxygen vacancy on surface structure. From this result, it revealed that increasing of surface defect can enhance photoactivity of titania. However, surface defect not only controlled activity, but also bulk defect. Enhancing of surface defect can be performed by increasing of %O<sub>2</sub> in N<sub>2</sub> or changing feed gas from O<sub>2</sub> to H<sub>2</sub>. Unfortunately, bulk defect increased by treatment in hydrogen atmosphere. Photoactivity of H<sub>2</sub>-treated titania was lower than O<sub>2</sub>-calcined titania.

### **12.1.4 Impact of surface defect (Ti<sup>3+</sup>) present in TiO<sub>2</sub> on the catalytic properties of the Co/TiO<sub>2</sub> catalyst**

This work showed impact of Ti<sup>3+</sup> present in titania support on characteristics and catalytic properties of Co/TiO<sub>2</sub> catalysts on methanation. The present of Ti<sup>3+</sup> in titania support increased with increasing of %O<sub>2</sub> in feed during calcinations process. The amounts of Ti<sup>3+</sup> present in titania support apparently affected on characteristics of Co/TiO<sub>2</sub> catalyst. Cobalt dispersion increased with the amounts of Ti<sup>3+</sup> present in titania because of enhancing of strong interaction degree. EDX analysis showed that oxygen vacancy site enhanced with the present of Ti<sup>3+</sup> in titania support. Reduction behavior of Co/TiO<sub>2</sub> catalyst also changed due to Ti<sup>3+</sup> present in titania support. It showed that high reducibility occurred when more Ti<sup>3+</sup> was present in supports. The various Co/TiO<sub>2</sub> samples were tested for their activities for the methanation. The unchanged CH<sub>4</sub> selectivity of the Co/TiO<sub>2</sub> samples were observed. It can be concluded that strong interaction arising from the present of Ti<sup>3+</sup> in titania support can enhance conversion of CO on methanation without changing CH<sub>4</sub> selectivity.

### 12.1.5 Effect of surface sites ( $\text{Ti}^{3+}$ and $\text{Ti}^{4+}$ ) of $\text{TiO}_2$ support on the formation of cobalt-support compound in $\text{Co/TiO}_2$

In this work, the effect of surface species (as a  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$  on  $\text{TiO}_2$  support) on the cobalt-support compound formation (Co-SCF) has been investigated on the  $\text{Co/TiO}_2$  catalyst. It revealed that the Co-SCF preferred to form on  $\text{Co/TiO}_2$  catalyst when the most proportion surface site of  $\text{TiO}_2$  support became  $\text{Ti}^{4+}$ . Based on ESR spectra, it was demonstrated that the Co-SCF had a simple chemical form as a  $\text{Co}^0(\text{H}_x\text{TiO}_y)$ . This compound reached to be a higher non-uniform structure when the number of  $\text{Ti}^{4+}$  on  $\text{TiO}_2$  surface increased. These are the promising knowledge that should be used to develop the characteristics of  $\text{Co/TiO}_2$  catalyst especially the formation of Co-SCF. The number of  $\text{Ti}^{4+}$  should be decreased as much as possible to prevent the formation of such the compound. It might be done treating the  $\text{TiO}_2$  surface prior to preparing the  $\text{Co/TiO}_2$  catalyst.

### 12.1.6 Effect of surface defect ( $\text{Ti}^{3+}$ ) and bulk properties on $\text{TiO}_2$ nanocrystal on its crystal growth rate during high temperature treatment

In this work, a study on the main parameter influencing the crystal growth rate of crystalline  $\text{TiO}_2$  during high temperature was developed using three kinds of crystalline  $\text{TiO}_2$  obtained from sol-gel (based on precipitation process), sol-gel (based on peptization process), and solvothermal synthesis. Using the interpretation coinciding with the impact of initial crystallite size of  $\text{TiO}_2$ , it was shown that the crystallinity (impurity, bulk defect), surface defect ( $\text{Ti}^{3+}$ ), hydroxyl ions in structure, and densification were not the main parameters controlling crystal growth rate, but the initial crystallite size ( $d_0$ ) of  $\text{TiO}_2$  was. It should be further noted that this conclusion was valid only in the nano-level. Based on the knowledge from this work, the surface defect ( $\text{Ti}^{3+}$ ) can be created as much as required in order to improve the photo and chemical properties of crystalline  $\text{TiO}_2$  without any further significant effects on the crystal growth rate during high temperature.

### 12.1.7 Probing surface defect ( $\text{Ti}^{3+}$ ) on $\text{TiO}_2$ nanocrystal with $\text{H}_3\text{Re}_3(\text{CO})_{12}$

The IR, EPR, and EXAFS data reported here form the basis for a schematic representation of the surface chemistry of hydroxylated anatase. According to this picture, during evacuation at 773 K, defect sites are formed on hydroxylated titania as either (a) a bridging OH group is removed, forming two neighboring  $\text{Ti}^{3+}$  sites, or (b), when a  $\text{Ti}^{4+}-\text{O}$  bond is cleaved, forming a  $\text{Ti}^{3+}$  site and an  $\text{O}^-$  species, with the  $\text{Ti}^{4+}-\text{OH}$  group being converted into a  $\text{Ti}^{3+}-\text{OH}$  group. When the probe molecule  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  is adsorbed on a titania surface with  $\text{Ti}^{3+}$  defect sites, it reacts preferentially with these sites, becoming deprotonated, removing most of the oxygen radicals, and healing the defect sites.

### 12.2 Recommendation

In this study, the defect on the surface of  $\text{TiO}_2$  nanocrystal was investigated, however, as known that the defect inside the bulk also plays the important parameter affecting to the properties of  $\text{TiO}_2$  nanocrystal. Therefore, we recommend that the controlling of bulk defect and the relationship between surface and bulk defect and its applications should be studied in the future research.