CHAPTER 4

CONCLUSIONS

4.1 Preparation and characterization of pure TiO_2 and V, Cu, Fe-doped TiO_2 by the modified sol-gel method and the impregnation method

The modified sol-gel process has been developed to synthesize high-purity TiO_2 with a high degree of reproducibility. XRD patterns of anatase TiO_2 indicated that the position and intensity of characteristic peaks of the samples were confirmed with the JCPDS file no. 21-1272 at 400-900 °C. The rutile phase appeared in XRD peaks when calcined at the temperature 800 °C and was confirmed with the JCPDS file no. 76-318. The transformation of anatase to rutile increased with higher calcination temperature of 700-800 °C was also demonstrated in XRD peaks. The specific surface area of TiO_2 anatase was found to be 121 m^2/g at the calcination temperature of 400 ºC. The average pure TiO_2 sizes were found to be 15 and 60 nm at calcination temperature of 400 ºC and 700 ºC for 3h, respectively. All TEM images indicated TiO_2 having almost spherical shape.

The transition metal ions (V, Cu, and Fe) doped TiO_2 and Fe-doped TiO_2 have been successfully prepared by the modified sol-gel method and the impregnation method, respectively. TiO_2 doping photocatalyst with V, Cu, Fe ions shifted the absorption onset of the semiconductor to visible region. The doping with V, Cu, and Fe created in subband resulted in narrowing the band gap. The narrow band gap energy caused an easiness for excited electron to transfer from valence band to conduction band. Hence, narrow band gap energy could use the low energy to excite electron or produce electron and hole. The BET specific surface area increased with increasing amount of V, Cu, Fe-doped TiO_2 and decreased with higher amount of 2 at.% of V and 5 at.% of Cu-doped TiO_2. The large specific surface area could enhance photocatalytic activity. However, the higher amount of dopants decreased the specific surface area. BET equivalent diameter of V, Cu, Fe-doped TiO_2 decreased with increasing the amount of dopants content and increased with higher amount of 2 at.% of V and 5 at.% of Cu-doped TiO_2. The changing of specific surface area verified by the substitution of V^{4+}, Cu^{2+}, Fe^{3+}, and Ti^{4+} ions to form solid solution. V^{4+}, Cu^{2+}, Fe^{3+} ions could substitute Ti^{4+} ion because the ionic radii of V^{4+}(0.61 Å), Cu^{2+}(0.59 Å), Fe^{3+}(0.64 Å) were similar to that of Ti^{4+} ion (0.68 Å). XRD patterns of anatase TiO_2 and V, Cu, Fe-doped TiO_2 indicated that the position and intensity of the characteristic peaks of the samples were well conformed to the JCPDS file no. 21-1272. The XRD patterns of V, Fe, Cu-doped TiO_2 were identified as anatase predominant phase. The transition metal ions did not have an effect on the anatase-rutile phase transformation of the titanium dioxide. The peaks of transition metal ion could not be seen in the XRD patterns due to the small amount of transition metal ions in TiO_2 lattice. The broader or sharper of XRD peak could be related to the particle sizes. TEM images of V, Cu, Fe-doped TiO_2 in the anatase phase demonstrated their almost spherical shape. The average particle sizes of V, Cu, Fe-doped TiO_2 were in the range of 10-20 nm at calcination temperature of 400 ºC. The particle sizes of V, Cu, Fe-doped TiO_2 was obtained from TEM measurement match quite well with the BET equivalent diameter was obtained from BET calculation. Elemental surface composition and oxidation state of elements were examined by using XPS. The peaks were characterized by a narrow width which indicated that the Ti existed as Ti^{4+}. Fe-doped TiO_2 samples were characterized by the binding energy indicated as typical of Fe^{3+}. TiO_2 photocatalyst doping with vanadium, iron, and copper shifted the absorption onset of the semiconductor to the visible region. Dopants introduce energy levels into the band gap, which are responsible for the red shift of the intrinsic absorption edge of TiO_2 and of the enhancement of visible light absorption. The recombination rate was decreased by the presence of ions acting as electron or hole traps. However, as presented the red shift observed was ineffective to completely mineralize organic compounds under visible light illumination but the good photoactivity depended on many factors such as type, concentration of dopants, and high specific surface area.

The Fe-doped TiO_2 was prepared by the impregnation method with a high degree of reproducibility. The impregnation method has many advantages such as the actual amount of doping iron on TiO_2 and the preparation was easy for preparing the doped catalysts. When doping with iron under the same amount of Fe dopant, it could be seen the different color of the powder obtained by the impregnation method and by the modified sol-gel method. The color of Fe-doped TiO_2 prepared by the impregnation method was dark reddish color, while Fe-doped TiO_2 prepared by the modified sol-gel method was less reddish at the same amount of iron. The doping TiO_2 photocatalyst with iron shifted the absorption onset of the semiconductor to the visible region. The samples prepared by the modified sol-gel and the impregnation method have uniform small particle sizes, high specific surface area, which possibly lead to higher photocatalytic activity.

4.2 Photocatalytic activity of pure TiO_2 and V, Cu, Fe-doped TiO_2 prepared by the modified sol-gel method and the impregnation method

The efficiency of mineralization was studied in organic compounds as: sucrose, phenol, oxalic acid, formic acid, methanol, and malonic acid under near UV, solar light, and visible light irradiations. Mineralization of oxalic acid with 500 μg of carbon using TiO_2 calcined at 400 °C for 3h showed the highest activity under near-UV irradiation. Under UVA and solar spectrum light illumination, pure TiO_2 outperformed all doped TiO_2 photocatalysts in mineralizing organic compounds. The optimum concentration of Fe-doped TiO_2 was 2 at% of iron prepared by the modified sol-gel method showed a superior performance in mineralizing oxalic acid under visible light illumination. Cu-doped TiO_2 mineralized about 10% of the oxalic acid, while no significant mineralization of oxalic acid was observed in the V-doped TiO_2 sample under visible light illumination. Although Cu could form complex with oxalate, the low mineralization extent indicated that this complex could not be readily photolyzed to generate CO_2 under low energy illumination. The optimum concentration of 2 at.% of Fe-doped TiO_2 was prepared by the impregnation method also showed the highest activity for mineralization of oxalic acid under visible light irradiation.

Metal cations can increase the oxidation rate by participating not only in heterogeneous pathways but also in alternative Fenton-type reactions that produced additional $OH^{\bullet}$. The enhanced performance observed for the Fe-doped TiO_2 system was likely due to the formation of ferrioxalate complex that could be photolysed to CO_2 under visible light illumination, rather than the red shift of the Fe-doped TiO_2. Also, the complexation could be formed in Fe-formate, Cu-oxalate, and Cu-formate but their complexation did not enhance the photoactivity under visible light. It could be possible that: (i) the greater efficiency of Fe^{3+} may be due to the ability of Fe^{2+} to migrate away from the particle into solution, preventing the deleterious back-reaction; in contrast, Cu^0 was immobilized on the particle, (ii) Cu^{2+} acted positively or negatively, depending on the concentration. Cu^{2+} increased the rate, but a larger amount was detrimental or Cu^{2+} showed a negative effect at all concentrations, attributed to the fact that the short-circuiting of the cupric ion (iii) direct oxidation of Fe-formic acid was expected to be a slow efficient process because it caused the formation of a highly unstable $H^{\bullet}$ radical in solution. Many studies reported that doping TiO_2 with transition metals could shift the absorption onset, therefore increase the band gap energy of the semiconductor and retard the recombination of e^- and h^+ pair. However, as presented here the red shift observation was ineffective to completely mineralize organic compounds under visible light illumination.

The enhancement of photocatalytic activity depends on many factors such as particle size, surface area, amount of OH surface groups, crystallinity, and band gap. However, the preparation method is one the most important parameters for the best photoactivity. Moreover, photoactivity of doping materials depending on the type of transition metal ions doping, calcination temperature and the concentration of transition metal ions as reported by many researchers [1, 10, 97].

4.3 Suggestions for future work

4.3.1 Other dopants such as anion-doped (with N or S) TiO_2 will be further investigated by the modified sol-gel method for photocatalytic activity under visible light.

4.3.2 Preparation of pure TiO_2 and doped TiO_2 by using other method such as hydrothermal method will be further investigated for photocatalytic activity.

4.3.3 Photocatalytic activity of pure and doped-TiO_2 with organic compounds and dyes will be further investigated.