Chapter 5

Summary

The undoped TiO_2 sample and the trivalent (Al, B)-doped TiO_2 samples were prepared by the sol-gel technique at relatively low temperature (95^oC) from the hydrolysis and condensation reaction of titanium tetrachloride ($TiCl_4$) and then neutralized by ammonia solution until the pH value was 7. Then these products were characterized by several techniques such as XRD, BET, FT-IR, TGA, DTA, SEM, TEM, UV-Vis, and WDXRF spectroscopy techniques. The XRD spectrum of the synthesized TiO_2 indicated that the undoped TiO_2 sample contained only rutile phase. For Al-doped TiO_2 samples, some of these samples were anatase phase and also found a mixture consisting of anatase and rutile phases. In addition, the XRD results showed Al peak when higher amount of Al dopants were added. In the case of B-doped TiO_2 samples mixed phase of anatase and rutile phases were obtained. From the XRD measurement the information on the size of anatase and rutile crystallites were also obtained by using the Scherrer formula which indicated that the crystallite sizes were in nanometer scale. The broad and weak peaks in XRD spectrum of these synthesized samples indicated that predominantly amorphous phase being present in the sample as nanocrystalline sizes. The higher calcination temperature increase the crystallite size of the samples and also increase the content of anatase and rutile in samples. The surface area of the trivalent (Al, B)-doped TiO_2 samples have higher surface area than that of the undoped TiO_2 sample and commercial P25 TiO_2 sample due to lower crystallinity of the synthesized samples. The increasing calcination temperature resulted in decreasing surface area due to increasing crystallinity. The porous nature of synthesized titanium dioxide samples were studied by nitrogen adsorption isotherm indicated that the pore size is in the mesoporous and microporous regions for most of the trivalent (Al, B)-doped TiO_2 samples. In the case of the calcined samples showed only the mesoporous region. The FT-IR spectrum showed the presence of H_2O and NH_4^+ presumably on their surfaces and also Ti-O band which corresponding to anatase and rutile structure. The general formula of both synthesized TiO_2 thus can be written in the mixed form as TiO_2 for anatase or rutile crystalline and also $[Ti(H_2O)_x(OH)_2]^{2+}$ for amorphous phase. This summary help explain that both samples have low crystallinity and yet high content of amorphous. The results of TGA analysis of synthesized

sample indicated that these trivalent (Al, B)-doped TiO_2 samples showed the greater weight loss than the undoped TiO_2 sample implies that there was larger amount of hydroxyls as free water and impurity in sample. Data from DTA analysis of these as-prepared samples, showed the endothermic peak around 100^{o}C assigned to the expulsion of free water from samples. This was in confirmation with the TGA analysis which showed a greater weight loss in the trivalent (Al, B)-doped TiO_2 samples as compared to that in the undoped TiO_2 sample. An endothermic peak at around 250^{o}C associated with the removal of water from the network. The exothermic peak at around 400 ^{o}C (Al-doped TiO_2 samples), 450 ^{o}C (B-doped TiO_2 samples), 550 ^{o}C (undoped TiO_2 sample) indicated the phase transformation of TiO_2 gel from amorphous to anatase. The phase transformation from anatase to rutile appears around 800^{o}C (undoped TiO_2, and B-doped TiO_2 samples),and the exothermic peak in the range 850-1110 ^{o}C for Al-doped TiO_2 samples. A resulting from the formation of corundum peak for all Al-doped TiO_2 samples. The area of peak could also suggest the content of amorphous in these synthesized samples. It could be seen that the exothermic peak of Al-doped TiO_2 samples and some of B-doped TiO_2 samples show the area of peak larger than the undoped TiO_2 sample. This mean that these synthesized trivalent (Al, B)-doped TiO_2 samples containing more amorphous than the undoped TiO_2 sample. The SEM image indicated that the undoped TiO_2 sample appears lower aggregation of spherical shape particle than the trivalent (Al, B)-doped TiO_2 samples and also have uniform structure. But for Al-doped TiO_2 samples and B-doped TiO_2 samples, they appear as dense and smaller particle with highly aggregate than the undoped TiO_2 sample. For calcined samples, the high calcination temperature give larger dense sample than non-calcined sample. The TEM images showed the undoped TiO_2 sample only consisted of tenuous fibers of rutile while Al-doped TiO_2 samples, show highly aggregate of ball-like particles and also have small amount of tenuous fibers of rutile. In the case of B-doped TiO_2 samples, results of TEM images consisted of ball-like of anatase and also rod-like structure of rutile. The UV-Vis diffused reflectance study indicated the adsorption edge of Al-doped TiO_2 samples were lower than that the undoped TiO_2 sample, except some calcined_Al/TiO_2 samples having equal or more than the absorption edge of the undoped TiO_2 sample. In the case of B-doped TiO_2 samples, these onset of absorption were lower than the undoped TiO_2 sample, but calcined_B/TiO_2 samples show higher onset of absorption than that the undoped TiO_2 sample. The position of the absorption edge for most of the trivalent (Al, B)-doped TiO_2 samples are blue-shifted in comparision with the undoped TiO_2 sample due to the quantum-size effect. The studies of the band-to-band transition

showed that these synthesized titanium dioxide samples were fitted to the direct bandgap transition. From XRF spectrum of these synthesized titanium dioxide samples showed that contained trace amount of S, Si, and residual Cl (besides the two main elements : Ti and Al) for the data of Al-doped TiO_2 sample and contained trace amount of Ca, S, and Si element (besides the main elements : Ti) for the data of B-doped TiO_2 sample.

The photodegradation of methylene blue (MB) was investigated by using these as-prepared trivalent (Al, B)-doped TiO_2 samples, undoped TiO_2 sample, and commercial P25-TiO_2 sample under UV irradiation. In mixing TiO_2 catalysts with MB solution for the photocatalysis experiments, the adsorption of MB on the catalyst surface was allowed for 1 h to reach their equilibrium adsorption in the dark prior to irradiation with UV light, reflecting the extent of adsorption of MB molecule on the surface of these as-prepared TiO_2 catalysts. The results from the photocatalytic experiment at different irradiation time (1.5, 3.0, 4.5, and 6.0 h) are shown to gradually decrease in the term of remained of MB solution (C/C_o) monitoring at wavelenghts 614 nm and 656 nm. These results indicated that all synthesized trivalent (Al, B)-doped TiO_2 samples have lower photocatalytic efficiency than that commercial Degussa P25-TiO_2 catalysts.