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Synthesis and characterization of visible light active photocatalytic TiO_2

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Abstract

Using thermal hydrolysis and hydrothermal treatment, photocatalytic TiO_2 powders were synthesized. During the synthesis, the addition of other transition metals such as iron, copper, etc., affected the photocatalytic capability of synthesized powders, and enabled the activation by visible light. To enhance photocatalytic capacity of gas phase decomposition, the rate-determining adsorption rate of pollutant gases were improved via surface modification of TiO_2 powders. The surface modifiers were implanted using mechanochemical synthesis of dopants and photocatalytic powders.

Key Words : Photocatalysis, TiO_2, surface modification, gas phase decomposition

1. Introduction

Recently, the environmental problems on earth were issued greatly; therefore, the researches about ecology friendly materials or decompositions of pollutants were studied on many cases. Among those, in many numbers of the researches on photocatalytic properties of TiO2 were undergone, and the products using its photocatalytic effect were fabricated[1-4] due to not only its higher photocatalytic effects but also its various applications on industrial products, such as white base on pigments and electronic devices. By adding additional properties like photocatalytic effect, the usages of TiO_2 materials were expanded to the other areas.

Conventional powder preparation methods for photocatalytic TiO_2 were limited to solid-state reactions and wet chemical methods. From the solid-state reaction, the photocatalytic property of powder was not good enough to replace current applicable materials, and for the wet chemical methods, powder after powder preparation was amorphous nature. Therefore, wet chemical methods were required to thermal treatment at high temperature. During the calcinations and solid-state reaction processes, the properties of initial powder cannot be maintained. In this research, hydrothermal method, which can crystallize and synthesize without sacrificing initial properties of powders with certain extent[5-6], were applied to prepare visible light active photocatalytic TiO_2. In addition, hydrothermal method can easily dope other elements, which in this case were transition metal salts, on TiO_2 base. Hydrothermally treated powder was compared to the one prepared by conventional powder synthesis, such as emulsion method on basic characteristics and photocatalytic properties.

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2. Experimental Procedures

The experiments were undergone in two

ways: initial powder preparation and hydrothermal treatment. To prepare TiO_2 precursor powder, thermal hydrolysis of titanium oxysulfate was used. The mixtures of 0.05M of $TiOSO_4$ and 1.8M of urea were placed at under 10℃ for 3 to 7 hours and heated up to 90℃ for 30min at pH 7 to 8. Precipitated powder was fully dried at 80℃ for 2 to 6 hours in vacuum oven. To compare initial powder synthesis method, the hydrolysis of titanium iso-propoxide was used. In one batch, 0.12M of titanium iso-propoxide and 0.5g/l of HPC (hydroxypropyl cellulose) was mixing in 100ml of octanol solvent, and in the other batch, 0.48M of de-ionized water was mixed in 100ml of acetonitrile solvent. After 30 minutes of mixing, the both solvent was combined and maintained about 30 minutes to complete the hydrolysis reaction. To separate hydrolyzed powder from solvent, centrifuging the solution at 3000 rpm for 15 minutes and the sediment powder was washed with ethanol and dried at 100℃ for 3 hours.

Precursor powder was ball-milled for 2 hours, and sampled about 5g into de-ionized water. Well-mixed solution was placed in autoclave, and hydrothermally treated at 150℃, 200℃, and 250℃ for 3 hours. To synthesize visible-light active photocatalytic powder, during hydrothermal treatment, iron and copper nitrates were added, and its amount was 0.5 wt% of synthesized iron-copper doped TiO2 powder.

The powder from emulsion method was crystallized by the calcination method at 600℃ for 2 hours.

XRD (Rigaku, D/max-RB, 12kW, Cu Ka) and SEM (Philips 515) analyses were carried out on synthesized powder for basic powder properties. To characterize photocatalytic property, the decomposition of ethanol was used. 1g of final powder were placed in 200ml of ethanol solution with exposing at ultraviolet lamp (254nm, 18.4W). The amount of remained ethanol was confirmed by liquid chromatography (HP 1090M). To measure the decomposition capacity of exhaust gases by the synthesized powder, CO, NO2, and propane gases were introduced in the specially designed reaction chamber with the powders under the illumination of ultra violet ray (254nm, 18.4W). The amount of each gas was determined by gas chromatography (HP 6890).

3. Results and Discussion

The size of precursor powder from thermal hydrolysis was about 0.9㎛ and amorphous structure. In addition, the size of the emulsion method was about 2.5㎛ and amorphous. The powder shape was spherical, but after conventional calcination, heating up to 600℃ for 2 hours was aggregated and rugged. The size of the powder from thermal hydrolysis after calcination was shrunk to 0.8mm due to evaporation of organic compound like urea, and crystalline structure was anatase TiO2, which showed no trace of doped components. After calcination, the size of the emulsion method was 2.1㎛ due to evolution of large amount of organic materials, which were used to synthesize. Fig. 1 shows the SEM images of before and after calcination of TiO_2 powder from thermal hydrolysis. Fig. 2 shows the SEM images of before and after calcination of TiO_2 powder from the emulsion method. Fig. 3 shows the XRD analysis of precursor powders.

After hydrothermal treatment, the size of powders was 0.8㎛, and their crystalline structure was changed from anatase, anatase and rutile mixture, and rutile, as the treatment temperature went higher. Particle size distribution shows mono-dispersed and reduced average size due to the recrystallization during the treatment. In Fig. 1, the SEM image of treated powders is shown.

Using the decomposition of ethanol, the photo-catalytic properties of visible-light active TiO_2 and un-doped TiO_2 that had undergone identical preparation process except the addition of iron and copper salts was determined. The photocatalytic effect of visible-light active TiO_2 was about two times better than the un-doped

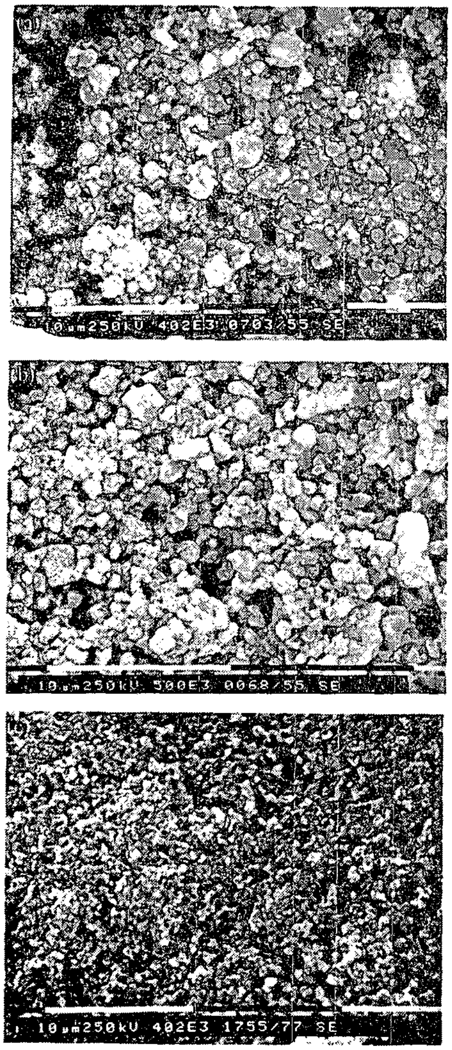

Fig. 1. SEM images of powders that were prepared by (a) thermal hydrolysis of $TiOSO_4$ at 90℃ for 30min., (b) calcined at 600℃ for 2 hours, and (c) hydrothermally treated at 150℃ for 3 hours.

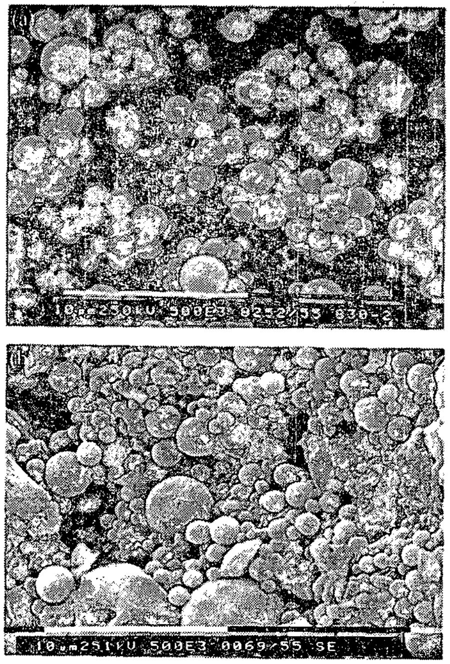

Fig. 2. SEM images of powders that were prepared by (a) hydrolysis of titanium iso-propoxide and (b) calcined at 60 0℃ for 2 hours.

one (Fig. 4). By the doping of iron and copper in TiO2 base, transition level was created within the band gap of TiO_2, and it means that less energy is required to activate photocatalysis. In addition, comparing the conventionally prepared TiO_2, which was synthesized using sol-gel method (0.12M of titanium iso-propoxide and 0.48M of deionized water with 0.1g/l of HPC), and hydrothermally treated one, the hydrothermally treated powder shows better photocatalytic properties about 1/4 times. From SEM images of both cases, the hydrothermally treated powder shows mono-dispersed and spherical shape. Photocatalysis is dependant on surface reaction between pollutant and TiO_2 surface, therefore morphology of powder can determine the amount of decomposition.

Using exhaust gas from automobile, the decomposition capability of the synthesized powder was determined. In Fig. 5, the decomposition rate on the various pollutants with synthesized TiO_2 powder was shown. From these results, carbon monoxide is most difficult to decompose, and ethanol is the easiest one. This inclination agrees to the formation energy of pollutants.

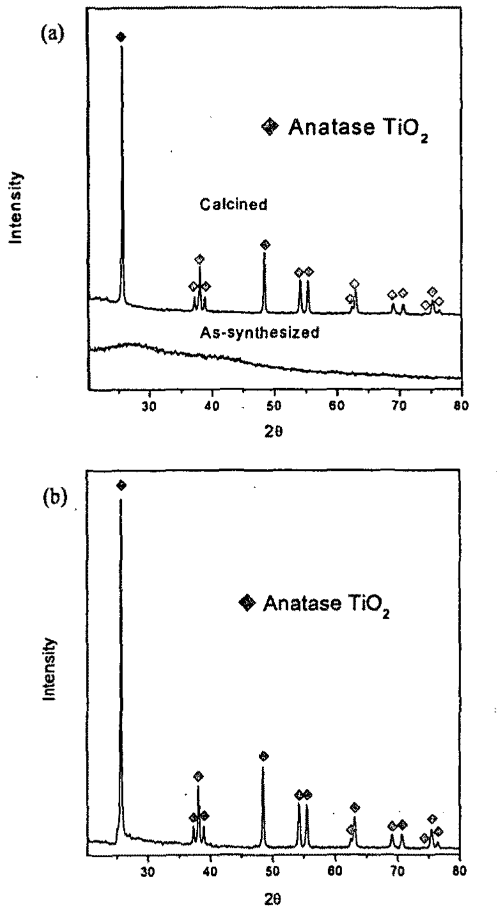

Fig. 3. XRD analysis of the powder from the (a) emulsion method and (b) thermal hydrolysis.

4. Conclusions

Using hydrothermal treatment and adding transition metallic salts, the photocatalytic properties of TiO_2 was increased. Using hydrothermal treatment, the morphology of powder was improved, and from this improvement, the efficiency of photocatalytic effect was increased. Via hydrothermal treatment, the doping of transition metal in TiO_2 base can be achieved without high temperature process. The doping of transition metals in TiO_2 base produce intermediate levels between TiO_2 band gap, and make possible to beactivated by visible light.

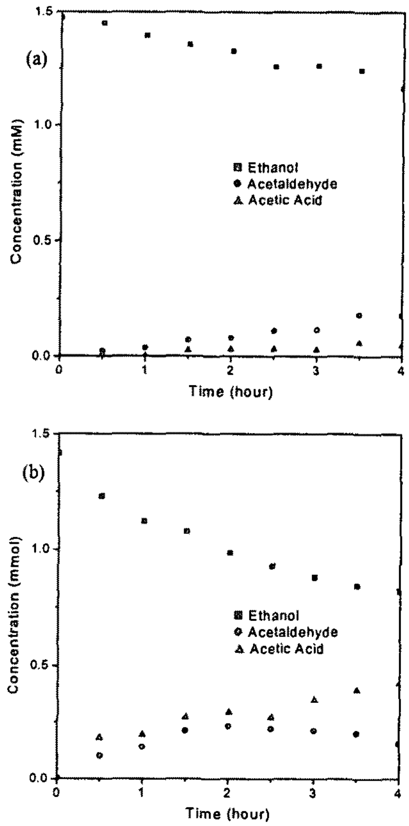

Fig. 4. Effect on the decomposition of ethanol by (a) un-doped TiO_2 and (b) Fe-Cu doped TiO_2.

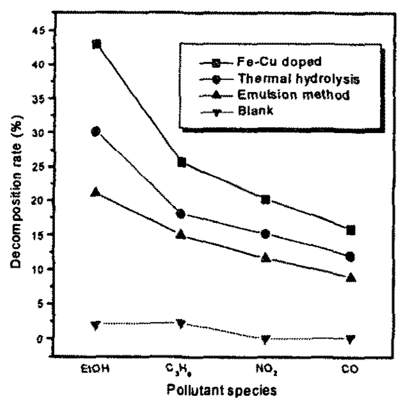

Fig. 5. Decomposition rate of various pollutants with synthesized TiO_2 under the illumination of UV lamp (254nm, 18.4W)

Acknowledgments

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