Jang, H. D., Lee, J. C., Kil, D. S., Synthesis of titania nanopowder and its photocatalytic properties.
International Symposium on the Fusion Technology of Geosystem Engineering, Rock Engineering and Geophysical Exploration
Seoul, Korea, Nov. 18-19, 2003

Synthesis of titania nanopowder and its photocatalytic properties

Hee Dong Jang, Jae Chun Lee, Dae Sup Kil
Korea Institute of Geoscience and Mineral Resources, Daejeon, Korea

Abstract: Titanium dioxide (TiO_2) nanoparticles were prepared by the oxidation of titanium tetrachloride ($TiCl_4$) in a diffusion flame reactor. The average diameter of particles was 15 to 30 nm and mass fraction of anatase ranged from 40 to 80 %. Effects of particle size and phase composition of those TiO_2 nanoparticles on photocatalytic properties such as decomposition of methylene blue and bacteria gas were investigated. The degree of decomposition of methylene blue by the TiO_2 nanoparticles under the illumination of the black light was directly proportional to the anantase mass fraction, but inversely to the particle size. The decomposition of bacteria by the TiO_2 nanoparticles under the illumination of the fluorescent light showed the same trend as in the case of the methylene blue.

1. Introduction

In recent years, applications to the environmental cleanup have been one of the most active area in photocatalysis. This is inspired by the potential application of TiO_2-based photocatlaysts for the destruction of organic compounds in polluted air and wastewaters (Ollis and Al-Ekabi, 1993) because TiO_2 nanoparticles have high photoactivity on the decomposition of organic materials, and chemically stable properties, etc. There are many variables that affect the photoactivity such as particle size, crystal structure, incident light intensity, pH of solution, and preparation method of TiO_2 nanoparticles (Fotou et al., 1994; Lee et al.,1992; Kominami et al., 1997). Crystal structure and particle size are considered as important factors that determine photoactivity. In this work, TiO_2 nanoparticles having different phase compositions and particle sizes were prepared by the gas phase oxidation of titanium tetrachloride ($TiCl_4$) in a flame reactor. The effect of the particle size and phase composition of TiO_2 nanoparticles on the photocatalytic properties such as decomposition of methylene blue and bacteria were investigated quantitatively.

2. Experimental

Preparation of TiO_2 nanoparticles

A scheme of the experimental apparatus for the generation of TiO_2 nanoparticles is shown in Fig. 1. A diffusion flame burner (3.4 cm in outside diameter and 45 cm in length) composed of five concentric stainless tubes was installed. A quartz tube of 10 cm in diameter and 120 cm in length was also installed to preserve the flame and particles. Liquid phase $TiCl_4$ was injected to the evaporator by using the syringe pump. Hydrogen (H_2) was used as a fuel while oxygen (O_2) and air as oxidants. The particle morphology and size were observed by transmission electron microscopy (TEM, Philips Model CM12). The average particle diameter was determined by counting more than 200 particles from TEM pictures (Jang, 1997). The specific surface area of the powders was measured by nitrogen adsorption at −196℃ using the BET equation (Micrometrics Model ASAP 2400). X-ray diffractometer (XRD, Rigaku Co. Model RTP 300 RC) was used to analyze X-ray diffraction patterns. The phase composition of TiO_2 particles was calculated from relative intensities of the strongest peaks corresponding to anatase and rutile (Spurr and Myers, 1957).

Determination of Photocatalytic Properties

Decomposition of methylene blue ($C_{16}H_{18}ClN_3S$) was determined by a photocatalysis evaluation checker (PEC, Ulvac Co., Model PCC-1). PEC consists of a light emitting element and receiving element that are connected to a black light (UV quantity about 1 mW) by means of a fiber. The absorbance change (ΔABS) between two elements with decomposition of colored film (methylene blue) by photocatalysis can be determined relatively with PEC. Large absolute value of the ΔABS means the high decomposition of methylene blue by photocatalyst. Experimental procedure was as follows; Thin TiO_2 film was prepared with coating solution including TiO_2 nanoparticles (0.1

wt%) on the surface of stainless steel plate. TiO_2 coated plate was covered with methylene blue solution of 1mmol/L by dipping, and dried for 2 hours. Then, the decomposition of methylene blue was measured by PEC.

Escherichia coli was chosen to determine the decomposition of bacteria. The growth in the number of each bacteria without addition of TiO_2 nanoparticles under the illumination of a fluorescent light (UV quantity about 1 μW) was measured with the lapse of time. After the addition of 0.1 gram of TiO_2 at the known number of bacteria, the change of the number of bacteria was measured with the lapse of time under the illumination of fluorescent light.

3. Results

Preparation of TiO_2 nanoparticles

For the preparation of TiO_2 nanoparticles having different particle sizes at the constant anatase mass fraction, $TiCl_4$ concentration in the flame was varied from 8.90 x 10^{-6} to 5.54 x 10^{-5} mol/l by changing the feed rate of $TiCl_4$ at the maximum flame temperature of 1700℃. Gas flow rates of the burner to synthesize the TiO_2 particles are as follows; 1^{st} : 2 l/min of Ar, 2^{nd} : 5 l/min of Ar, 3^{rd} : 6 l/min of H_2, 4^{th} : 15 l/min of O_2, and 5^{th} : 60 l/min of air. As $TiCl_4$ concentration increased, the specific surface area decreased from 102 to 50 m^2/g. The average diameter obtained from TEM picture was 13nm at 8.9x10^{-6} mol/l and increased 28nm at 5.54x10^{-5} mol/l. Figure 2 shows TEM image of TiO_2 nanoparticles generated at 8.9x10^{-6} mol/l of $TiCl_4$ concentration. From the analysis of X-ray diffraction patterns the crystalline phases of the TiO_2 nanoparticles generated from different $TiCl_4$ concentrations were found nearly the same; it was 45% anatase in mass fraction.

In order to change anatase mass fractions keeping particle size constant, $TiCl_4$ concentration and gas flow rate at the 4^{th} and 5^{th} tube of the burner were varied. As the oxygen flow rate decreased from 15 to 5 l/min at fixed total gas flow rates, and 2.27 x 10^{-5} mol/l of $TiCl_4$ concentration, the average particle diameter also decreased from 23 to 14 nm. The maximum flame temperature was lowered from 1700 to 1400℃ along with decreasing the oxygen flow rate. The anatase mass fraction of TiO_2 nanoparticles increased from 41 to 80 % as the oxygen flow rate decreased from 15 to 5 l/min. When 10 l/min of air was introduced into the 4^{th} tube of the burner while holding the constant total gas flow rates and 2.27 x 10^{-5} mol/l of $TiCl_4$ concentration, the average particle diameter of product particles was 14 nm and anatase mass fraction was 61%. When the total gas flow rate was changed from 65 to 70 l/min by decreasing the air flow rate at 5^{th} tube of the burner, particle size and anatase mass fraction were 15nm and 48%, respectively.

Determination of Photocatalytic Properties

Figure 3 shows the effect of particle size on the decomposition of methylene blue at the constant phase composition of TiO_2 (45% anatase). As the particle size decreased, the ΔABS increased. The decomposition of methylene blue by the commercial TiO_2 nanoparticles (Degussa, P25, average diameter is 25 nm, and the phase composition is 75% anatase) was also measured for comparison. When the particle size was less than 23 nm, the ΔABS of methylene blue by TiO_2 prepared in the present study was a little higher than that by the P25. It was considered that the degree of decomposition became larger owing to larger surface area even though anatase mass fraction of synthesized powder was smaller than that of the P25.

The effect of the phase composition at the fixed particle size (15 nm) on the decomposition of methylene blue was also investigated. As the phase composition of anantase increased, the ΔABS of methylene blue also increased and the degree of decomposition became larger than that of the variation of the particle size. The degrees of the decomposition of methylene blue by TiO_2 nanoparticles having different phase composition were higher than that by the P25. From above results, the decomposition of methylene blue was affected by the particle size and anatase mass fraction. The effect of anatase mass fraction played more important role in enhancing the degrees of decomposition of methylene blue than that of particle size.

The initial numbers of bacteria (escherichia coli) prepared were about 400. The degree of decomposition of bacteria was observed after 30min, 1 hour and 3 hours. The number of bacteria was not changed after 1 hour. The effect of particle size keeping constant anatase mass fraction (45%) on the decomposition of the escherichia coli was found to be 93.2 % at the particle size of 30nm and 97.6% at the particle size of 15nm, respectively. As the anatase mass fraction increased from 45 to 80%, the degree of decomposition of the escherichia coli also increased from 97.6 to 99.1%. Figure 4 show the image of escherichia coli before and after the addition of TiO_2 nanoparticles to the bacteria. As previously stated, the decomposition of bacteria with P25 was observed for comparison; it was 98.6% for the escherichia coli. From this result, it was found that TiO_2 nanoparticles having smaller size and higher anatase mass fraction were more effective on the decomposition of the bacteria under the illumination of very low intensity of UV light, and anatase mass fraction was much more effective on the decomposition of the bacteria than the particle size.

4. Conclusions

Photocatalytic TiO_2 nanoparticles having various particle size and phase composition were prepared through the control of $TiCl_4$ concentration and gas flow rate in the diffusion flame reactor; the particle size ranged from 15 to 30nm and anatase mass fraction from 45 to 80%. Photocatalytic properties TiO_2 nanoparticles such as decomposition of methylene blue, bacteria and ammonia gas were investigated in terms of the particle size and anatase mass fraction. As the particle size decreased and anatase mass fraction increased, higher degree of decomposition of methylene blue by the TiO_2 nanoparticles under the illumination of the black light was obtained. The higher degree of decomposition of bacteria and ammonia gas by the TiO_2 nanoparticles under the illumination of the fluorescent light were found at the smaller particle size and the higher phase composition of anatase. The effect of anatase mass fraction played more important role in enhancing photocatalytic properties than that of particle size.

References

Fotou, G. P., S. Vemury, and S. E. Pratsinis, 1994, Chem. Eng. Sci., 49, 4939.
Jang, H. D., 1997, AIChE Journal, 43, 2704.
Kominami, K., J. Kato, Y. Takada, Y. Doushi, and B. Ohtani, 1997, Catal. Lett., 46, 235.
Lee, W., Y. Gao, K. Dwight, and A. Wold, 1992, Mat. Res. Bull., 27, 685.
Ollis, D. F. and H. Al-Ekabi, 1993, Eds, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam.
Spurr, R. A., and H. Myers, 1957, Anal. Chem., 29, 760.

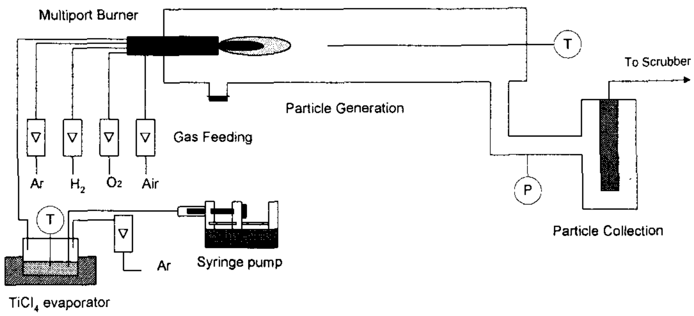

Fig. 1. A schematic of experimental apparatus for the synthesis of TiO_2 nanoparticles.

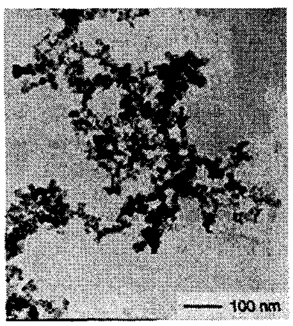

Fig. 2. TEM image of TiO_2 nanoparticles synthesized in the present study.

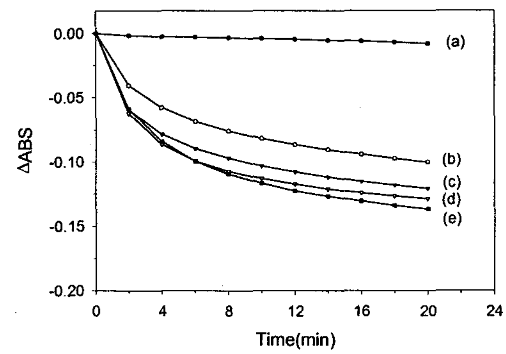

Fig. 3. Effect of particle size of TiO_2 nanoparticles the decomposition of the methylene blue ((a): without TiO_2, (b): dp=30, (c): dp=26, (d) dp=23, (e) dp=15nm).

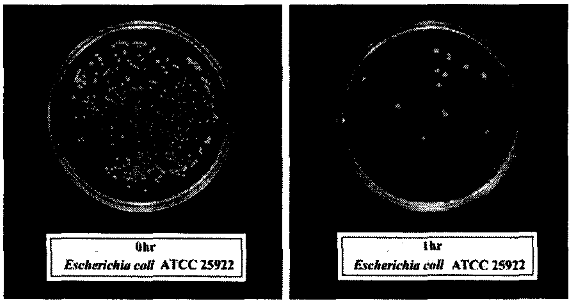

Fig. 4. Images of escherichia coli before and after the addition of TiO_2 nanoparticles into the bacteria