Preparation of dip-coated TiO_2 photocatalyst on ceramic foam pellets

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In recent decades, the photocatalytic reaction has attracted a great deal of attention for the purification of aquatic or atmospheric environments [1, 2]. Especially, titanium dioxide (TiO_2) has been widely utilized as a photocatalyst for generating electrons (e^-) and holes (h^+), thereby inducing reductive and oxidative reactions, respectively. The electrons and holes can be excited through UV light irradiation to overcome the band gap energy. Accordingly, O_2^- and OH $\cdot$ radical ions are produced and mineralize pollutants into CO_2 and H_2O. The highly oxidative ability of photocatalysis is very effective in the detoxication of volatile organic carbon (VOC) pollutants such as phenol. In this case, VOC passes through various reaction steps. The photo-oxidative reaction mechanisms and the mineralization pathway for the photoreaction of phenol are described schematically in Fig. 1.

For deriving an effective photocatalytic reaction, suspended TiO_2 particles have been conventionally used. However, there are significant problems such as particle handling and solid/ liquid separation, so TiO_2 materials coated on solid supports have been actively studied to overcome these disadvantages. This study proposes a unique and economical coating technique: the dip coating of micro-dimensional TiO_2 particles onto ceramic foam pellets with a thickness of several millimeters. The ceramic foams also feature a high porosity (about 80%) but a large pore size (about 100 μm), and so facilitate the dip-coating with TiO_2 particles to produce a photocatalytic reaction with a high efficiency at low cost. In the final section of this letter, we report an experiment on the photodegradation of phenol using prepared pellets with dip-coated TiO_2.

The pellets support materials to be coated, were prepared by the following three major processes: slurry preparing, foaming, and pelletizing. These processes have been reported in earlier literature [4, 5]. The raw material for the ceramic foam pellets was silica powder of about 3 μm in particle size. The pellets undergoing the final pelletizing process were sifted for constant size in the range 3 to 5 mm, and for close to spherical shape. The porosity estimated from bulk, square-shaped, ceramic foams was measured to be about 77%; the specific surface area using BET (NOVA 1000, Quantachrome, USA) was about 2.04 m^2/g; and the mean pore diameter using scanning electron microscope (SEM) photographs (JSM-6300, JEOL, Japan) system was about 107 μm.

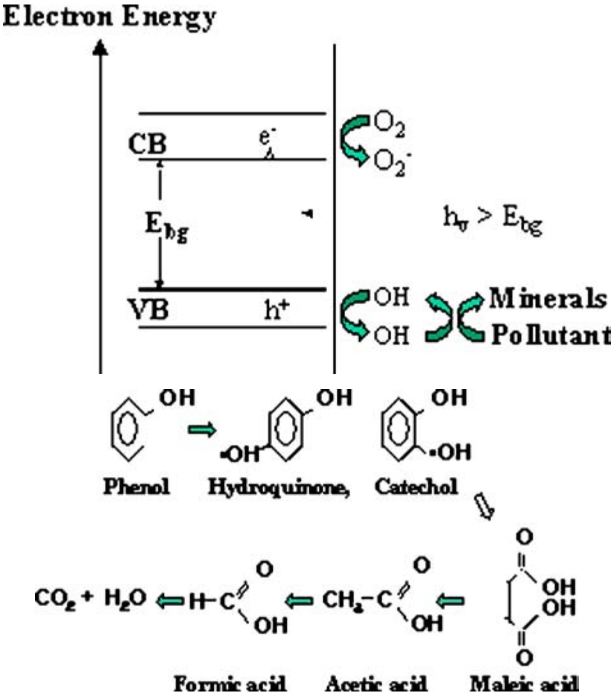

Figure 1 A schematic diagram of mechanisms for the photocatalysis (a) and the photocatalytic mineralization (b) of phenol.

After preparation of the supporting pellets, TiO_2 particles were coated according to the principle of thermodynamic spontaneous attachment onto the pellet surfaces. The coating suspension consisted of distilled water, polymer dispersant (Darvan 7, R.T. Vanderbilt, USA), and TiO_2 powder of 1.05 μm in average particle size, which was measured using a particle sizer (Sald 2001, Shimadzu, Japan). A surface electrical property assessed by the zeta potential meter (Zetasizer 2000, Malvern, USA) showed that there might be favorable attachment between them, due to their different kinds of surface charges around pH 5 (Fig. 2).

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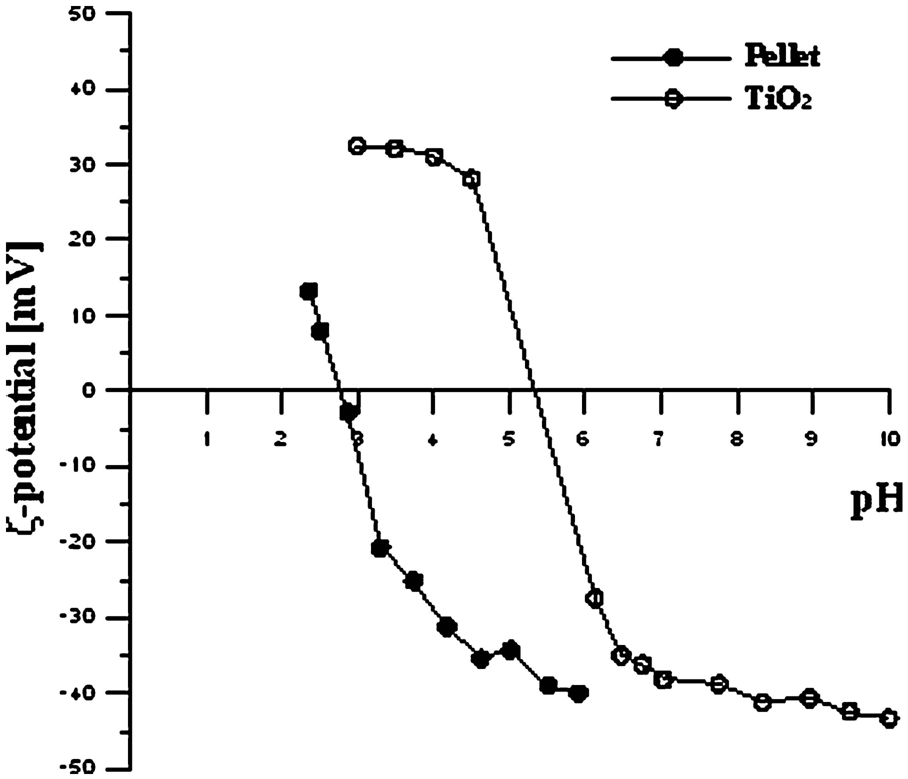

Figure 2 ζ-potentials of a pellet and TiO_2 according to pH.

In spite of the spontaneous attachment, the coating of TiO_2 suspension may be hindered by its high viscosity at a high concentration of the particles in the suspension. Thus, particle concentration and the corresponding viscosity of the suspension were checked using a spectrometer (Hach 2010, Hach, USA) and viscometer (UV II+, Brookfield, USA).

As a result, concentrations less than 5 wt.% or greater than 15 wt.% were found to be inappropriate to form enough coating layers on the pellets, because of insufficient attachment capacity and excess viscosity, respectively. The optimal concentration was determined to be 10 wt.% for a sound coating, and the optimal concentration of dispersant was similarly determined to be 5 wt.%. For an even spread of coating slurry throughout the pellet pores, pressure in the pores was lowered to 0.3 atm for 2 h.

A chemical analysis using ICP (Optima 3000 DV, Perkin Elmer) revealed that the volume of coated TiO_2 particles on a pellet occupied as much as 10 wt.% of the whole volume of the pellet. This suggests that the coating suspension was uniformly filled throughout all pores, when it is considering that the slurry penetrating pores contain only 10 wt.% TiO_2 in the slurry. SEM photographs of an uncoated pellet and one coated with TiO_2 particles are compared in Figs 3 and 4, respectively.

In addition, it is necessary to examine the change of the crystal structures according to calcinating temperature [1, 2]. TiO_2 contains small band gap energies, 3.2 eV for anatase phase and 3.0 eV for rutile phase. Even the higher energy, anatase phase, shows a higher photocatalytic efficiency than the rutile because anatase is constructed of a highly activated structure. The ratio between the amounts of phases present in the coated TiO_2 can be estimated by the peak ratio produced from an X-ray diffractometer (XRD, DMAX III, Rigaku, Japan), according to the following mathematical formula for the peak ratio (*f*):

$$f = \frac{1}{1 + 1.26\frac{I_A}{I_R}} \qquad (1)$$

where f is weight fraction of the anatase present, and I_A and I_R are the intensities of primary peaks for anatase and rutile, respectively. Table I shows calculated *f* values for coated and uncoated TiO_2, and the specific surface area of coated TiO_2, according to heating temperature. Under normal conditions, the anatase phase is converted into rutile phase at 800 °C. For the Ti-O-Si bonding of this study, a temperature of 1000 °C is required for the corresponding transition [2]. The *f* values of coated TiO_2 with heating temperatures of 500 and 600 °C are relatively low because of insufficiently developed crystallization. The values of the specific surface area of coated TiO_2 show that the number of

TABLE I *f* values calculated by Equation 1, and specific surface area of TiO_2-coated pellets

	f		
Heating temperature (°C)	TiO_2 powders	TiO_2 coated layer	Specific surface area(m^2/g)
500	78	64	6.2
600	70	69	6.5
700	46	75	4.2
800	0	30	4.9
1000	0	0	1.4
1200	0	0	1.3

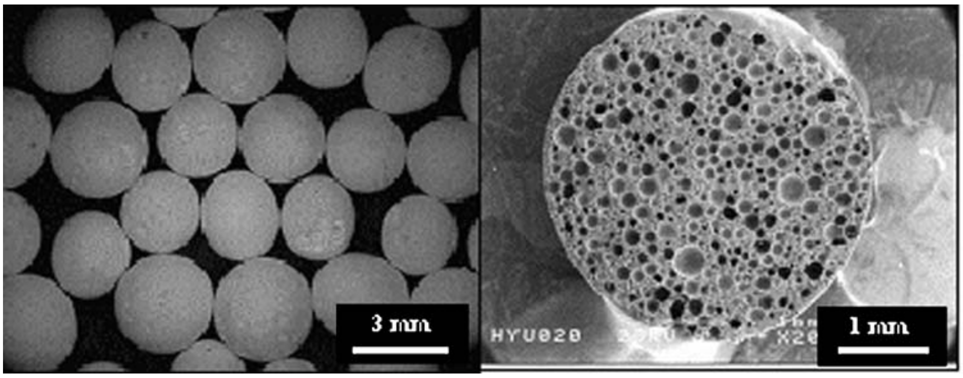

Figure 3 Appearance (a) and cross-sectional area (b) of ceramic foam pellets.

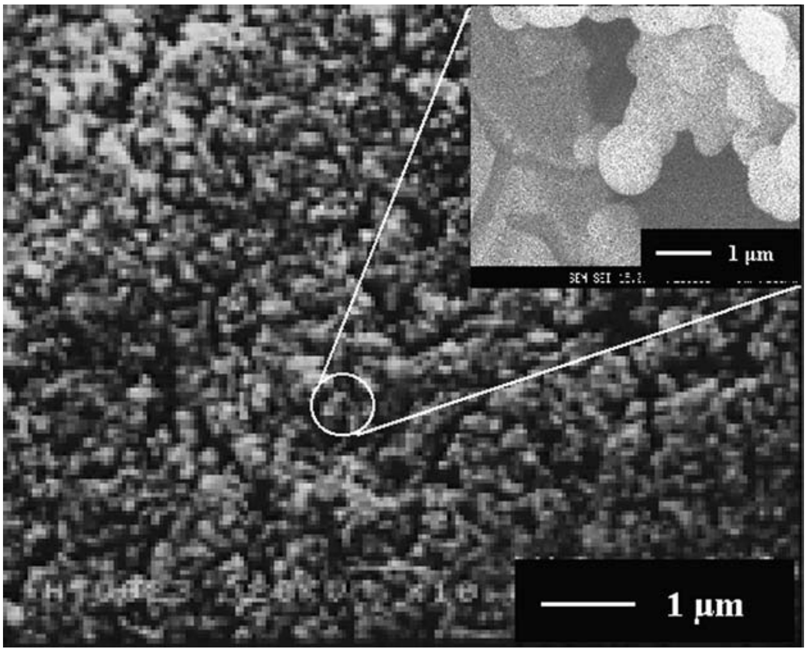

Figure 4 SEM photographs of TiO_2 coated on ceramic foam pellet.

reactive sites decreases as the conversion from anatase to rutile progresses.

Finally, to estimate the photocatalytic effectiveness of the prepared, dip-coated TiO_2 particles, the experimental reactions with phenol degradation were executed with shaking for homogenization during the reaction. The phenol of 99.9% purity used in the experiment is a commercial product (Kumho P& B, Korea). A UV light source ($G_{20}T_{10}$, Sanky Denki, Japan) can radiate photoenergy of 68.7 $\mu W/cm^2$ at 1 m distance with a wavelength of 250 nm. The concentration of phenol was measured by using the spectrometer, after the distillation preprocessing using a Liebig's condenser.

Fig. 5 presents the first-order photo-degradation of phenol as a function of irradiation time, with variations of heat temperature. The kinetic expression of phenol removal is described as follows:

$$C = C_0 \exp(-kt) \quad (2)$$

where C is the concentration of phenol in a reactor; C_0 is the initial concentration of phenol; k is the photocatalytic reaction constant; and t [s] is the reaction time. k [s^{-1}] values obtained by fitting experimental data were 1.76×10^{-2}, 2.92×10^{-2}, 2.63×10^{-2}, 1.18×10^{-2}, 0.49×10^{-2}, and 0.29×10^{-2} s^{-1}, for TiO_2 photocatalyst with heating temperatures of 500, 600,

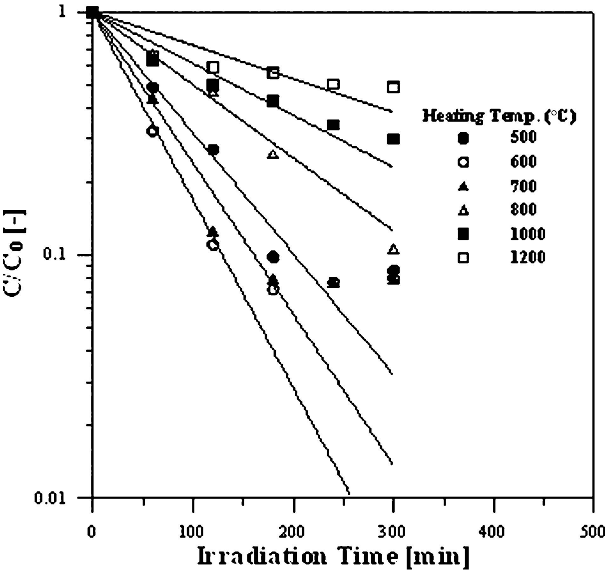

Figure 5 Photo-degradation of phenol according to the irradiation time in the presence of TiO_2-coated pellets.

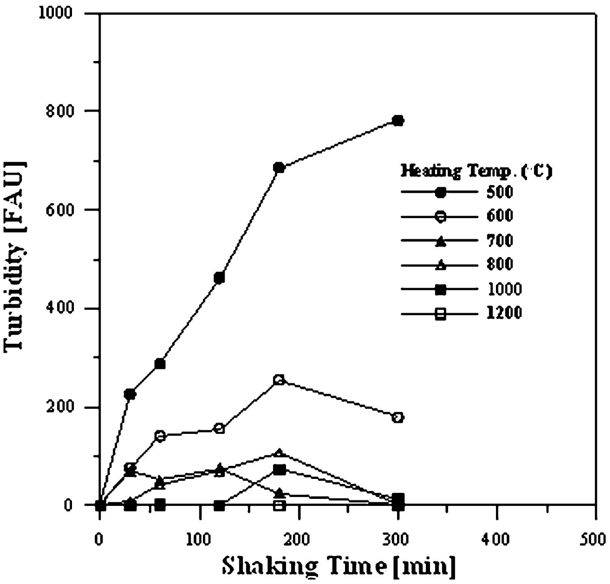

Figure 6 Variation of turbidities according to shaking time for TiO_2-coated pellets.

700, 800, 1000, and 1200 °C, respectively. It should be noted that the variation of k values is in accordance with that of the specific surface area of coated TiO_2; refer to Table I. For evaluating coating adhesion of TiO_2 powders on the pellet surface, 5 g of coated pellets were agitated at 120 rpm in 100 cm^3 water using the rotation of a shaker (Jeio Tech, Korea). In the case of the reaction with TiO_2 at 500 and 600 °C heating temperatures, many particles were detached from the surface of the pellets and the water turbidity increased, due to a lack of heat treatment of the coating (Fig. 6). When compared with the effectiveness of the uncoated TiO_2 particles (1 μm in size) whose k values ranged from 0.55×10^{-2} s^{-1} to 2.33×10^{-2} s^{-1}, the dip-coated TiO_2 photocatalyst with heating temperatures of 600 and 700 °C showed a higher efficiency in photodegradation of phenol. On the other hand, heat treatment at temperatures greater than 800 °C was inefficient for phenol removal because of the decrease in specific surface area due to phase-transformation from anatase to rutile phase.

In conclusion, the dip-coating described in this study is advantageous because of its inexpensiveness and the ease of handling of the coating materials. However, there is such a shortage that the reticulate pore structure of the ceramic foam pellets may consume an excessive amount of TiO_2 for coating, because coated TiO_2 on the inner pore surface may not have photocatalytic activation. Nevertheless, the dip-coated TiO_2 showed a better phenol removal effect than the uncoated, at heating temperatures of about 700 °C.

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