Characterization of Stone Powder/TiO₂ Core/Shell Composite Particles Prepared from TiO₂ Nanoparticles via Heterocoagulation in a Water System

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Abstract: Stone powder (SP)/TiO₂ core/shell composites were prepared from SP and nano-crystalline TiO₂ sols as the core and shell particles, respectively, via heterocoagulation. The dispersion stability of the particles has been investigated, on the basis of the DLVO and heterocoagulation theories, as a function of the pH and concentration of surfactants. The core/shell composite particles were characterized as a function of the weight ratio of SP/TiO₂ by various techniques, such as XRD, FE-SEM, N₂ adsorption, ASC, and their photocatalytic activities for the decomposition of methylene blue (MB) in water. The optimum value of pH for the preparation of the SP/TiO₂ core/shell particles was 3.5. The homogeneous TiO₂ coating was obtained when the weight ratio of SP/TiO₂ was 80/20. The ASC and BET surface area of the prepared SP/TiO₂ (80/20) particles were 91% and 60.6 m²/g, respectively. The SP/TiO₂ core/shell particles, prepared by the heterocoagulation method, exhibited efficient photocatalytic activities toward the decomposition of MB, which was increased with respect to the UV irradiation time and the TiO₂ loading.

Keywords: stone powder, nano-TiO₂, core/shell composite, heterocoagulation

Introduction

Heterogeneous photocatalysis has a high potential in applications related to liquid phase pollution control processes. Among the metal oxide semiconductors applicable for photocatalytic processes, titanium dioxide (TiO₂) has been the one most commonly used, because of both its high photocatalytic activity and chemical/photocorrosion stability [1-3]. The efficiency of some commercial TiO₂ samples toward photooxidation has been fully evaluated, but the particle sizes are usually too small and the recovery of the catalysts is difficult, which limits their commercial applications. On this basis, a great effort has been made to develop supported titania catalysts, which offer large active surface areas and more convenient recovery. Titania-coated silica particles are of great interest for a number of potential applications, such as catalysts, white pigments (whiteners), and photonic crystals [4,5]. It is possible to increase the exposed number of active sites by coating titania on silica supports. In general, the methods used to coat silica with titania include impregnation, precipitation, microemulsion, heterocoagulation process, and sol-gel techniques [6,7]. Nano-sized TiO₂ or titania-coated silica particles have been prepared mainly by the sol-gel method. However, the major disadvantage of this approach is that it employs organic solvents, which are environmentally harmful (the molar ratio [R] of water/titanium alkoxide ≤4) [3]. Furthermore, high temperatures (≥400°C) are required for calcination to provide efficient photocatalytic activity. To overcome these disadvantages, we attempted to prepare water-based nano-crystalline TiO₂ sols (R ≈420) without calcination; this process can be applied to many kinds of core/shell composite particles. In particular, the heterocoagulation process is very simple and can be applied to a wide variety of materials without any significant difficulties [8]. One disadvantage of the process, however, is that it is not

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possible to form dense coatings and the adhesion forces are usually weak. In a previous study, we overcame the problem by coating nano-TiO₂ sol on monodisperse silica (Dₚ₀ₐ = 330 or 700 nm) [9]. We were interested in coating nano-TiO₂ sol on stone powders (SPs) having various particle sizes, rather than on monodisperse silica particles in a water system. However, such research has yet to be reported in the literature, as far as we know.

SP sludges are usually generated as by-products during the processing of stone panels, which causes malignant effects on the water, air, and soil, and even on the human body. To reduce such pollution and to recycle the by-products, various methods have been studied to process the materials into, for instance, artificial marbles and construction materials for housing [10]. The outcomes, however, have been insignificant.

In this research, SP/TiO₂ core/shell composites were prepared using SP and nano-crystalline TiO₂ sols as the cores and shells, respectively, via heterocoagulation in a water system. The dispersion stability of the prepared particles was investigated as a function of pH on the basis of the DLVO (Derjaguin-Landau-Verwey-Overbeek) and heterocoagulation theories [11,12]. The core/shell composite particles were characterized, by altering the weight ratio of SP/TiO₂, using various techniques, such as X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), low-temperature N₂ adsorption, apparent surface coverage (ASC), and the photocatalytic activity for the decomposition of methylene blue (MB) in water.

**Experimental**

**Materials**

Titanium tetraisopropoxide (TTIP, 99%, Junseii), CTAB (cetyltrimethylammonium bromide, BDH Co.), nitric acid, ethanol, and isopropyl alcohol (IPA) were used as received. The SP sludges were collected as a by-product during panel processing of Hwangdeung Stone (Iksan, Korea). The SP sludges were washed and then dried at 70°C. The chemical composition of the SP sludges is shown in Table 1. Doubly distilled water was used for all experiments.

**Preparation of Materials**

**Nano-titania Sol**

A solution of TTIP in C₂H₅OH was added dropwise (2 mL/min) to a solution of H₂O, C₂H₅OH, and HNO₃ at room temperature. The molar ratio of H₂O, C₂H₅OH, and HNO₃ to TTIP was fixed at 420:2:0.2. The hydrolysis reactions started immediately upon mixing, as indicated by the rapid increase in turbidity and the formation of large, visible flocs, which precipitated at the bottom of the reaction vessel. The reaction conditions were maintained under vigorous stirring (1000 rpm) for another 30 min to attain equilibration of the reactions (hydrolysis and particle formation). Subsequently, the peptization reaction was maintained for a period of 12 to 72 h at 80°C until a clear white-blue solution was observed, which indicated the resuspension of the precipitates and reduction of the particle size. Finally, the resultant sol was heated at 220°C for 12 h, to produce a monodisperse nano-TiO₂ sol with crystallization of anatase in an autoclave.

**SP/TiO₂ Core/Shell Composite Particles**

SP/TiO₂ core/shell composite particles having different compositions were prepared by the heterocoagulation method, according to the following procedures. The SPs (Dₚ₀ₐ = 3.1 μm, 1.0 g/L) were dispersed homogeneously in an aqueous solution (1 mM KCl) using an ultrasonic homogenizer. The pH of the dispersion (250 mL) was adjusted as desired using KOH or HCl. The resultant dispersion was poured into a 500-mL round-bottom flask and stirred (250 rpm) at 25°C for 1 h. Thereafter, at a given pH (3.0, 3.5, or 4.0), a desired amount of nano-TiO₂ sol was added dropwise (2 mL/min) and then the mixture was stirred at 25°C for 8 h. The prepared composite particles were filtered, washed, and dried at 70°C.

**Measurements**

The particle size distributions of the prepared particles were determined using a particle size analyzer (UPA-150, Microtrac). The morphology of the particles was observed by FE-SEM (S-4700, Hitachi). The XRD patterns were obtained using a Rigaku X-ray diffractometer. The diffractograms were measured at values of 2θ in the range 10 to 60°, using a CuKα incident beam (λ = 1.5418 Å) monochromated by a nickel filter. The scanning speed was 4°/min, and the voltage and current of the X-ray tubes were 40 kV and 30 mA, respectively. The zeta potentials of the prepared particles were measured using an electrophoresis instrument (ELS-800, Otsuka Electronics Co.). An electrolyte solution (1 mM KCl) was used to keep the ionic strength constant while the pH was varied by adding 0.01 N HCl or KOH into the dispersion. The pH of the dispersion was taken as the isoelectric point (IEP) when the zeta potential was zero.

The ASC of the TiO₂-on-SP particles was calculated on the assumption that the molecular weight of SP is equal to that of silica and using the following equation [14]:

\[
% \text{ASC} = \frac{M_T (\text{IEP}_{SP} - \text{IEP}_{SP/γ})}{M_S (\text{IEP}_{SP/γ} - \text{IEP}_{SP})} = \frac{M_T (\text{IEP}_{SP} - \text{IEP}_{SP/γ})}{M_S (\text{IEP}_{SP} - \text{IEP}_{SP/γ})}
\]

where \( M_T \) and \( M_S \) are the molecular weights of titania and SP, respectively. The subscripts SP, Ti, and SP/Ti
Table 1. Chemical Composition of SP [13]

<table>
<thead>
<tr>
<th>composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>MnO</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>67.6</td>
<td>17.2</td>
<td>3.99</td>
<td>4.06</td>
<td>2.58</td>
<td>1.70</td>
<td>0.57</td>
<td>0.81</td>
<td>0.49</td>
<td>0.27</td>
<td>0.10</td>
<td>1.20</td>
</tr>
</tbody>
</table>

refer to the stone powders, TiO₂ particles, and SP/TiO₂ core/shell composite particles, respectively.

The specific surface areas of the prepared particles were determined by nitrogen adsorption/desorption isotherms obtained at 77 K using a model ASAP 2010 (Micromeritics Instrument Corporation, USA). Prior to the measurements, all samples were degassed at 300°C and 1 × 10⁻³ torr for 3 ~ 6 h.

Photocatalytic Activities for the Decomposition of MB

To evaluate the photoactivity of the prepared samples, the decomposition behavior of MB in water was examined as follows. In an MB aqueous solution (500 mL; concentration, 10 ppm), sample powders (0.25 g) were dispersed under ultrasonic vibration for 5 min. The solution was circulated in an annular photoreactor (4 cm × 30 cm). After at least 15 min, the MB concentration in the solution was found to be constant for all of the samples prepared. Therefore, the solution containing the sample powders was kept in the dark for 30 min and then irradiated with UV light (UV lamp; 15 W; central wavelength, 254 nm). The concentration of MB in the solution was determined by measuring the absorbance of each aliquot (10 mL) at 660 nm as a function of the UV irradiation time after passing through a 0.2-µm membrane filter.

Results and Discussion

Dispersion Stability of TiO₂ Sol

The average particle size of the TiO₂ sol was measured to be 16.9 nm (S_{BET} = 257 m²/g). The zeta-potential and average particle size (D_{50}) of the TiO₂ sol were measured as a function of pH, and the results are shown in Figure 1. The zeta-potential of the TiO₂ sol decreased gradually upon increasing the pH of the solution, approached zero at pH 5.36, and then increased up to pH 10. The D_{50} of the TiO₂ sol increased gradually upon increasing the pH of the solution, approached 1360 nm at pH 5.36 (IEP), and then decreased up to pH 10. It can be expected that the stability of the sol at different values of pH is a direct consequence of the surface charge of the particles. The surface structure of the hydrous TiO₂ particles is ≡Ti-OH. When the pH of the aqueous solution is lower than the IEP, the surface structure is converted to the ≡Ti-OH⁺ form. When the pH of the aqueous solution is higher than the IEP, the surface takes the ≡Ti-O⁻ form. This behavior can be explained by the DLVO theory in consideration of the interaction potential energy among the TiO₂ particles [11,12].

![Figure 1. Effect of pH on the zeta-potential and average particle size of TiO₂ particles prepared by the hydrothermal method.](image)

The dispersion stability of the particles is particularly important because unwanted particles could aggregate during the complexation process. The stability can be assessed from the total potential energy curve, which is the sum of the van der Waals (mostly attractive forces) and electrostatic interactions (mostly repulsive forces) between the particles. The values of V_{T,max} (energy barriers) for the TiO₂ sols at different pH conditions are summarized in Table 1. The DLVO theory predicted that slow and rapid homoagglomerations can occur at pH 4.0 and 4.0 < pH ≤ 10.0, respectively, because the energy barrier falls to about 0.5 kT or less in this pH range. On the other hand, the stability of the sol was predicted to persist at pH ≤ 3.5 and pH ≥ 10 because the energy barrier was about 0.5 kT or higher. The value of the energy barrier for prevention of TiO₂ homoagglomeration was in good accordance with the former average particle size data as a function of pH (Figure 1). Rapid aggregation was expected to occur around the IEP of the shell particles, and, thus, we attempted to prepare the composite particles at pH 3.0, 3.5, and 4.0 where rapid aggregation cannot occur.

Characterization (Morphology, ASC Analysis, XRD Analysis, Specific Surface Area) of SP/TiO₂ Core/Shell Composite Particles

Figure 2 shows SEM images of the core/shell particle surfaces prepared from SP and TiO₂ in various weight ratios at pH 3.5, 250 rpm, and 25°C. The surface of the composite particles is rough and textured. The textured surface indicates that the SP core was coated by the
nano-TiO₂ particles. When the TiO₂ loading was > 20 wt%, aggregation of TiO₂ particles was observed. The degree of aggregation increased upon increasing the TiO₂ loading.

Figure 3 shows the pH dependence of the zeta potentials of SP, TiO₂ particles, and SP/TiO₂ particles. The zeta potential of each sample increased upon decreasing the pH of the solution; this finding can be explained by the shift of the acid-base equilibrium of the surface OH groups. The IEPs of the SP and TiO₂ particles are 2.8 and 5.36, respectively. The IEP of the SP is similar to that of SiO₂ particles (IEP = 2.6) [15]. This result is due to the similarity in the major chemical composition of SP (Table 1). This finding means that the surface acidity of SP is greater than that of TiO₂ particles in the aqueous solution. It should be noted that when the TiO₂ particles were coated on SP, the IEP changed significantly from 2.8 to 5.36, which is much nearer to the value of SP than that of TiO₂. It is clear from Figure 3 that the IEP of the SP/TiO₂ particles increased systematically and approached that of pure TiO₂ particles upon increasing the TiO₂ loading. The ASC of the SP/TiO₂ core/shell particles was measured as a function of the TiO₂ loading; the results are shown in Figure 4. The ASC increased exponentially upon increasing the TiO₂ loading up to 25 wt% and then it leveled off at higher loadings, regardless of pH. The ASC of the composite particles at a given TiO₂ loading increased in the following order of pH: 4.0 > 3.0 > 3.5. This result is due to the dispersion stability of the TiO₂ sols. The ASC values of the composite particles were <100% at pH 3.0 and 4.0. This result indicates that some of the particle surfaces remained uncoated even though some other particles were coated with multilayers of the TiO₂ particles. Moreover, the effect of pH on ASC is due to the loss of the pure or agglomerated TiO₂ particles, via draining out through the membrane filters, in the separation process of the composite particles because the TiO₂ sol was highly stable at pH 3.0 and the TiO₂ particles agglomerated at pH 4.0.

The IEP of the SP/TiO₂ (85/15 wt/wt%) particles prepared from titania modified with 1 mM CTAB was 11.3 (88.3% by ASC). The pre-treatment of TiO₂ particles
with CTAB had no effect on their ASC values, but it extended the pH region over which the composite particles could be prepared.

Figure 5 shows the XRD patterns of the TiO\textsubscript{2} SP, and SP/TiO\textsubscript{2} (50/50 wt/wt\%) particles treated at different calcination temperatures. When the calcination temperature was lower than 700°C, the major phase of the TiO\textsubscript{2} particles prepared by hydrothermal synthesis was pure anatase (i.e., without brookite). No noticeable peak of the rutile phase was observed at lower weight ratios of SP/TiO\textsubscript{2} (up to 50/50) or at any of the calcination temperatures. The SP/TiO\textsubscript{2} core/shell composites had high thermal stability, which led to suppression of the TiO\textsubscript{2} phase transformation from anatase to rutile. This result may be due to the presence of SiO\textsubscript{2} in the SP, because the radius of the Si\textsuperscript{4+} ion (0.40 Å) is smaller than that of the Ti\textsuperscript{4+} ion (0.61 Å).

The BET surface area of the SP/TiO\textsubscript{2} composite particles was measured as a function of the TiO\textsubscript{2} loading; the results are shown in Figure 6. The surface area increased upon increasing the TiO\textsubscript{2} loading, regardless of pH. The surface area of the SP/TiO\textsubscript{2} (80/20) composite particles prepared at pH 3.5 was 60.6 m\textsuperscript{2}/g, an increase of 640%, when compared to that of pure SP (9.4 m\textsuperscript{2}/g), but a decrease of 76% when compared to that of pure TiO\textsubscript{2}. This result indicates that the surface area of the composite particles can be controlled in accordance with the loading of the TiO\textsubscript{2} particles.

Methylene Blue Decomposition

In Figure 7, the relative concentrations (c/c\textsubscript{0}) of MB in solution as a function of irradiation time of UV light are shown for the SP/TiO\textsubscript{2} composites prepared at various TiO\textsubscript{2} loadings. Before UV irradiation, the sample solutions were kept in the MB solution for 30 min in the dark to saturate the adsorption of MB by the sample particles. The relative concentration of MB adsorbed on the SP/TiO\textsubscript{2} composites decreased exponentially upon increasing the irradiation time and the TiO\textsubscript{2} loadings. The results indicate that the SP/TiO\textsubscript{2} composites have good photocatalytic activities for the decomposition of MB. A relatively good linearity between c/c\textsubscript{0} and irradiation time was observed at up to 60 min for each sample. The rate constant k determined from these linear relations, for the composite particles containing 10 wt\% TiO\textsubscript{2}, was calculated to be $19.99 \times 10^{-3}$ min\textsuperscript{-1}, which is much higher than the blank test ($4.97 \times 10^{-3}$ min\textsuperscript{-1}). However, for the composite particles containing > 20 wt\% TiO\textsubscript{2}, the rate constant was about the same as that for the pure TiO\textsubscript{2} parti-
Table 2. Total Potential Energy Barriers of TiO₂ Particles (D₅₀ = 16.9 nm) in 1 mM Aqueous KCl Solution where the Hamaker Constant A = 5.35 × 10⁻²⁰ J

<table>
<thead>
<tr>
<th>pH</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
<th>4.5</th>
<th>5.36</th>
<th>6.0</th>
<th>8.0</th>
<th>9.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₅₀ [nm]</td>
<td>16.9</td>
<td>35.8</td>
<td>102</td>
<td>258</td>
<td>1360</td>
<td>1353</td>
<td>471</td>
<td>238</td>
<td>34.8</td>
</tr>
<tr>
<td>V̅_{min}[kJ/particle]</td>
<td>1.39</td>
<td>0.74</td>
<td>0.14</td>
<td>-0.28</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-0.30</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Note: "no energy barrier

Table 3. The Rate Constant and Decomposition Yield of MB in Solution at Various UV Irradiation Time Intervals in the Presence of SP/TiO₂ Composite Particles

<table>
<thead>
<tr>
<th>SP/TiO₂ (wt/wt%)</th>
<th>decomposition yield of MB (%)</th>
<th>rate constant k at ~ 30 min (×10⁻³, min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 30 min</td>
<td>at 60 min</td>
</tr>
<tr>
<td>blank test (only UV)</td>
<td>12.99</td>
<td>26.13</td>
</tr>
<tr>
<td>90/10</td>
<td>52.98</td>
<td>67.44</td>
</tr>
<tr>
<td>85/15</td>
<td>56.56</td>
<td>69.02</td>
</tr>
<tr>
<td>80/20</td>
<td>59.92</td>
<td>83.01</td>
</tr>
<tr>
<td>75/25</td>
<td>65.80</td>
<td>80.17</td>
</tr>
<tr>
<td>titania sol</td>
<td>68.23</td>
<td>86.76</td>
</tr>
</tbody>
</table>

Figure 7. Changes in relative concentration of MB (c/c₀) in the solution vs the UV irradiation time in the presence of the SP/TiO₂ (wt/wt%) composite particles, where c₀ and c are the initial and changed concentrations of MB, respectively.

Table 4. Comparison of the Photocatalytic Activities of SP/TiO₂ Composite Particles with and without CTAB

Conclusions

In a water system, SP/TiO₂ core/shell composites were prepared successfully from SP samples and nano-crystalline TiO₂ sols as the core particles and the shell particles, respectively, via heterocoagulation. The ASC and surface area of the prepared SP/TiO₂ composite particles increased upon increasing the TiO₂ loading. The treatment of TiO₂ particles with CTAB had no effect on the ASC, but it extended the pH region over which the preparation of the composite particles was feasible. The composite particles had high thermal stability, leading to the suppression of the TiO₂ phase transformation from anatase to rutile. The photocatalytic activities of the prepared SP/TiO₂ composite particles for the decomposition of MB increased upon increasing the TiO₂ loading. Therefore, the SP/TiO₂ core/shell particles prepared by the heterocoagulation method are expected to be utilized as, for example, white pigments, fillers, and photo-catalyst materials.

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References

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