Film-Coating Process of Hydrated Alumina on TiO₂ Particles

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The mechanism of the film-coating process of hydrated alumina on TiO₂ particles in aqueous solution was experimentally studied. pH and ζ-potential changes during the mixing process of the TiO₂ suspension and Al₂(SO₄)₃ solution were investigated. TiO₂ particles obviously promote the hydrolysis of Al₂(SO₄)₃ in both acidic and basic solutions and adsorb positively charged OH−Al species in slurries. A static repulsion dominates the suspension system of OH−Al species and TiO₂ particles, in which they randomly collide with each other because they carry the same sign of charge. When the OH−Al species or TiO₂ particles have enough energy to cross the repulsion threshold, the −OH groups on the surface of the TiO₂ particles will condense with the OH−Al species, leading to the coating of OH−Al species on the surface of the TiO₂ particles. However, completely inelastic collisions also occur between the OH−Al species, and the formation of hydrous alumina is unavoidable unless the local concentration of the coating reagent in the suspension is well controlled. The morphology and surface chemical states of coated TiO₂ particles were also analyzed by high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). TiO₂ particles coated with hydrous alumina exhibit electrokinectic behavior similar to that of pure Al(OH)₃ gel.

Introduction

Much attention has been focused on fine TiO₂ particles. They are excellent white pigments used in the paint, plastic, and paper industries for their unique advantages, including an outstanding refractive index, insolubility, and nontoxicity. However, TiO₂ particles are easily pulverized, and the polymer molecules in the paint film are easily cracked because of the strong photocatalysis activity of TiO₂ particles, especially when they are exposed to ultraviolet radiation, e.g., sunlight.[1] Consequently, the paint is easily scoured off and undergoes yellowing discoloration. These characteristics severely restrict the utilization of the excellent optical properties of TiO₂ particles.[2] To overcome these problems, TiO₂ particles need to be coated with a layer of a continuous, dense, and inert film to seal the TiO₂ particles and prevent pulverization and photocatalysis from occurring.[3]

A thin and uniform film coating can improve both the pigment weather durability and the optical properties. The optical properties of the pigment mainly depend on the crystal structure, particle size, composition, and surface morphology of the TiO₂ particles.[4] However, the uniformity and properties of an oxide coating influence the surface properties of the pigment particles, because the coated particles show similar surface characteristics, such as surface charge and surface-active sites or groups, as the coating materials.[1] Aluminum oxide is one of the most commonly used materials for the inorganic coating of TiO₂ particles. An aluminum oxide coating can enhance the amount of −OH groups on the particles, which improves the dispersibility of the powder in aqueous media and provides more active sites for organic modification.

A variety of chemical processes have been used for particle coating, e.g., alkoxide hydrolysis, metal hydroxide precipitation with ammonia, force hydrolysis of a metal salt in aqueous solution, and electrostatic adsorption.[5] The coating structure depends on the hydrolysis rate of the precursors. Amorphous nanosized particles are easily formed in a fast hydrolysis of the coating materials and are adsorbed on the core particles in the coating process.[6]

A good understanding of when and how coating materials form on the core particle surface is very important in many fields, especially in particle coating and catalyst preparation.[7] Many researchers[8,9] have used electrostatic attraction to explain the particle-coating process in aqueous solution, i.e., the core particle surface and the coating species carry opposite charges and are attracted to each other, leading to the adsorption of the coating materials on the core particle surface. Another proposed mechanism for particle coating is heterogeneous nucleation,[10] in which heterogeneous nucleation occurs prior to homogeneous nucleation and dominates in the coating process, because the critical concentration of precursors or coating materials to precipitate on the particle surface is lower than that for homogeneous nucleation. A mechanism of ion adsorption on the oxide surfaces is also found in the literature. When ions were adsorbed on oxide surfaces at high concentration, a transition from mononuclear adsorption to multinuclear adsorption occurs that finally leads to surface precipitation.[11,12] However, there is no detailed description of a proven mechanism for particle coating in the literature. This study investigates the coating mechanism of hydrous alumina on TiO₂ particles, which is based on the collisions among precursors and substrate particles followed by the condensation between them. The coating film structure and surface element composition and the electrokinetic behavior of the particles were analyzed by high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and ζ-potential analysis, respectively.

Experimental Section

Reagents. Commercial TiO₂ particles from the sulfate process, in which TiO₂ particles were produced from the hydrolysis of TiOSO₄ and subsequent calcination, were used in the experiments. The TiO₂ particles used were of rutile structure, 300 nm in mean diameter, and nonporous and had a BET surface area of 6.54 m²/g. Other chemicals used in the experiments were of analytical reagent (AR) grade.

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Coating Process. Experiments were carried out in a flask, in which the temperature and pH were measured online with a thermometer and a pH meter, respectively. TiO_2 particles, at a concentration of 100 g/L, were dispersed in deionized water with continuous ultrasonic treatment for 30 min prior to the titration of the $Al_2(SO_4)_3$ solution. Then, 0.3 mol/L of $Al_2(SO_4)_3$ solution and 1 mol/L NaOH solution were titrated into the TiO_2 suspension simultaneously. The TiO_2 suspension was stirred strongly and adjusted to a set pH by controlling the titrating speed of the NaOH solution, while the titrating speed of the $Al_2(SO_4)_3$ solution was kept constant. Samples were taken and analyzed at intervals to measure the surface charge and the morphology of the coated TiO_2 particles. After titration, the suspension was aged for 2 h with stirring. Then, coated TiO_2 particles were filtered, washed repeatedly until SO_4^{2-} was no longer detected using a $BaCl_2$ solution, and dried at 120 °C for 12 h.

Characterization. The ζ-potential of the particles was measured using a ζ-potential analyzer (ZetaPALS, Brookhaven Instruments, Holtsville, NY). The temperature during measurements was kept at 25 °C. The particle dispersion was enhanced by an ultrasonic treatment. Dilute solutions of HCl and NaOH were used for pH adjustment. The pH of each sample was measured rapidly with a pH meter before the ζ-potential measurement. The cell and pH electrode were carefully cleaned to avoid any possible contamination in each measurement. The final ζ-potential was the mean value averaged from three measurements.

The morphology and structure of the aluminum oxide coated TiO_2 particles were examined with a high-resolution transmission electron microscope (HRTEM, JEM-2011, JEOL Co., Tokyo, Japan). Samples for HRTEM inspection were dispersed in ethanol solution with ultrasonic treatment for 30 min. The chemical compositions and the binding energy of the atoms of the particle surface were determined by XPS (PHI-5300, Perkin-Elmer, Eden Prarie, MN).

Results and Discussion

The ζ-potential plays an important role in the particle-coating process.[9,10] However, it is not certain how the ζ-potential affects the coating process and when and how the coating process occurs. No proven mechanism for particle coating has been reported, especially for a hydrous alumina coating on particles because of the complexity of the OH−Al species.[13] To study the coating process of hydrated alumina on TiO_2 particles, experiments were carried out in this study. The change of pH and ζ-potential were investigated when an $Al_2(SO_4)_3$ solution was mixed with a TiO_2 slurry at different pH's.

1. pH Changes of the $Al_2(SO_4)_3$ Solution when TiO_2 Particles Are Introduced. The pH of the deionized water used in this experiment was 6.5, whereas the pH of the TiO_2 particles in the deionized water was 7.26. It is supposed that the TiO_2 particles adsorb H^+/H_3O^+ ions in the suspension because of the surface polarity of the TiO_2 particles, causing the pH to increase in the system. Five hundred milliliters of 4 g/L TiO_2 suspension was prepared for the experiment. The pH change of the $Al_2(SO_4)_3$ solution was investigated in the following experiments:

In one experiment, 25 mL of deionized water was put into each beakers A and B, and 0.15 mL of 0.03 mol/L $Al_2(SO_4)_3$ solution was added to each of the beakers. The dilute $Al_2(SO_4)_3$ solutions in beakers A and B were stirred with a magnetic stirrer, and the solution pH's in both beakers A and B naturally changed to the same value of 4.3 because of the hydrolysis of Al^{3+}. Then,

25 mL of deionized water was added to beaker A, whereas 25 mL of TiO_2 suspension was added to beaker B. After thorough mixing, the solution pH's were measured. If the solutions were just physically mixed or the TiO_2 particles did not affect $Al_2(SO_4)_3$ hydrolysis, the pH of the solution in beaker B should be higher than that in beaker A. However, the opposite result was obtained, as the solution pH in beaker B was 4.12, which was lower than the solution pH of 4.28 in beaker A.

The same phenomenon also occurred when the initial pH of the $Al_2(SO_4)_3$ solution was a high value. In this case, 25 mL of deionized water was put into each beakers C and D, and 0.15 mL 0.03 mol/L $Al_2(SO_4)_3$ solution and 0.25 mL 0.1 mol/L NaOH solution were added to each of these beakers under the same conditions. The solutions in beakers C and D were stirred with a magnetic stirrer, and the solution pH's in beakers C and D were measured to be the same at 8.8. Then, 25 mL of deionized water was added to beaker C, whereas 25 mL of TiO_2 suspension was added to beaker D. After thorough mixing, the solution pH's were measured. The solution pH in beaker D was 7.70, which was also lower than the solution pH of 8.13 in beaker C.

It can be inferred that the decreases in solution pH in beakers A and C resulted from the hydrolysis of the $Al_2(SO_4)_3$ solution, which was promoted when the $Al_2(SO_4)_3$ solution was diluted by deionized water. When the $Al_2(SO_4)_3$ solution was diluted by the TiO_2 particle suspension, i.e., beakers B and D, the solution pH decreased more, which might indicate a greater extent of hydrolysis. By analysis, $Al_2(SO_4)_3$ is the main reagent that can bring about a change in pH, as the hydrolysis of $Al_2(SO_4)_3$ releases H^+. The hydrolysis of the $Al_2(SO_4)_3$ solution can be expressed as follows,[14] where $Al(H_2O)_6^{3+}$ is denoted as Al^{3+}

$$Al^{3+} + H_2O = Al(OH)^{2+} + H^+ \tag{1}$$

$$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+ \tag{2}$$

$$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+ \tag{3}$$

$$2Al^{3+} + 2H_2O = Al_2(OH)_2^{4+} + 2H^+ \tag{4}$$

$$6Al^{3+} + 15H_2O = Al_6(OH)_{15}^{3+} + 15H^+ \tag{5}$$

$$7Al^{3+} + 17H_2O = Al_7(OH)_{17}^{4+} + 17H^+ \tag{6}$$

$$8Al^{3+} + 20H_2O = Al_8(OH)_{20}^{4+} + 20H^+ \tag{7}$$

$$13Al^{3+} + 34H_2O = Al_{13}(OH)_{34}^{5+} + 34H^+ \tag{8}$$
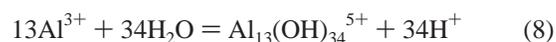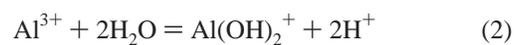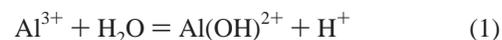
According to eqs 1−8, the introduction of TiO_2 particles into the $Al_2(SO_4)_3$ solution promotes the hydrolysis of $Al_2(SO_4)_3$, causing the H^+ concentration to increase and the pH to decrease. The TiO_2 particles promote the hydrolysis of $Al_2(SO_4)_3$ in both acidic and basic environments. The degree of pH decrease probably depends on the surface area and the charge carried by the TiO_2 particles. However, the detailed relation needs to be studied further in the future. To study how the TiO_2 particles promote the hydrolysis of $Al_2(SO_4)_3$, the ζ-potentials of the particles in beakers A−D were measured.

2. ζ-Potential of the TiO_2 Particles in the $Al_2(SO_4)_3$ Solution. The ζ-potential curve of pure TiO_2 particles and Al-$(OH)_3$ species at different pH values were measured and are presented in Figure 1. The Al(OH)$_3$ species was obtained from
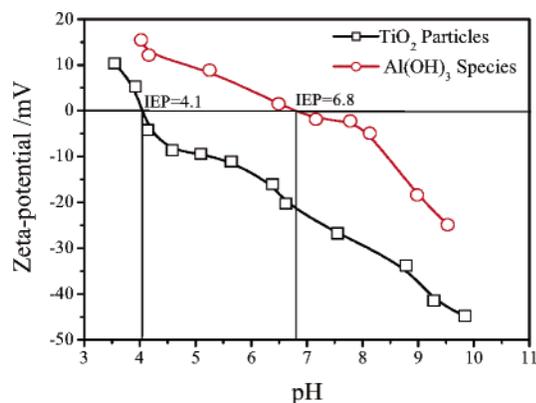
Figure 1. ζ-potential vs pH for pure TiO_2 particles and $Al(OH)_3$ species.

the hydrolysis of $Al_2(SO_4)_3$ at different pH values. The solution pH was adjusted with HCl solution to decrease the pH and with NaOH solution to increase the pH. Figure 1 shows that the isoelectric point (IEP) of the pure TiO_2 particles is about 4.1 and the IEP of $Al(OH)_3$ species is about 6.8.

TiO₂ particles carry different charges at different pH values, as indicated in Figure 1. The TiO_2 particle surface accepts or provides different amounts of protons at different pH's.[15,16] At lower pH, the concentration of H^+ is high, the TiO_2 particle surface accepts more protons from the water because of the surface polarity, and the TiO_2 particles carry a positive charge. At higher pH, the concentration of OH^- is high, the $-OH$ groups on the TiO_2 particle surface provide more protons to combine with the OH^- ions in the aqueous solution, and the TiO_2 particles carry a negative charge. When the TiO_2 particle surface provides the same amount of protons as it accepts, the TiO_2 particles carry no charge, corresponding to the isoelectric point.

From Figure 1, the ζ-potential of the TiO_2 particle suspension is almost 0 at pH 4.12 and about -25.0 mV at pH 7.70. The ζ-potential of the $Al(OH)_3$ species is 12.5 mV at pH 4.12 and -2.5 mV at pH 7.70. However, when the $Al_2(SO_4)_3$ solution and TiO_2 particle suspension were mixed, the ζ-potential was 18.8 mV at pH 4.12 and 7.5 mV at pH 7.70. This shows that the positive charge on the TiO_2 particles in $Al_2(SO_4)_3$ solution (beakers B and D) was not caused by the simple physical mixing of the $Al_2(SO_4)_3$ solution and pure TiO_2 particles.

When pH > pH_{iep}, the TiO_2 particles carry a negative charge, and H^+ ions are the main positive ions in the absorption layer according to DLVO theory.[17] When $Al_2(SO_4)_3$ solution is added, positively charged $OH-Al$ species and H^+ ions are the main counterions in the absorption layer, where a small quantity of negatively charged SO_4^{2-} and OH^- ions also exist. When $OH-Al$ species or H^+ ions condense with $-OH$ groups on the TiO_2 particle surface, the negative charge is permanently neutralized or reversed to positive charge. Therefore, when $Al_2(SO_4)_3$ solution is added to the suspension of TiO_2 particles, the ζ-potential of the TiO_2 particles is reversed from -25 to 7.5 mV.

When pH < pH_{iep}, the TiO_2 particles carry a positive charge, and OH^- ions are the main counterions in the absorption layer. When $Al_2(SO_4)_3$ solution is added, OH^- and SO_4^{2-} ions are the main counterions in the absorption layer, where a small amount of positively charged $OH-Al$ species and H^+ ions also exist. When $OH-Al$ species collide with TiO_2 particles through random collisions and break through the threshold of repulsion between them, condensation occurs between $OH-Al$ species and $-OH$ groups on the TiO_2 particle surface. Although there are more SO_4^{2-} and OH^- ions than $OH-Al$ species in the
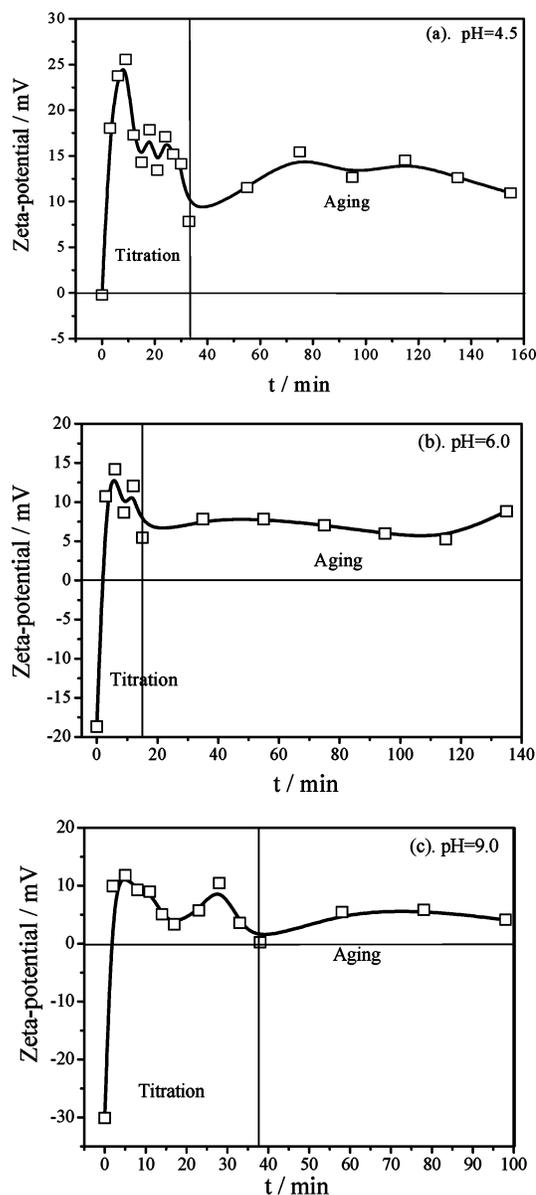
Figure 2. ζ-potential vs time during the titration and aging process, $T = 60$ °C. Titration: 0.3 mol/L $Al_2(SO_4)_3$, 0.3−0.5 mL/min. pH adjustment: 0.1 mol/L NaOH. (a) pH 4.5, (b) pH 6.0, (c) pH 9.0.

absorption layer, there is no condensation between them, and SO_4^{2-} and OH^- ions are not fixed in the coating layer. The $OH-Al$ species consumed in the absorption layer are supplied from the diffusion layer with the addition of $Al_2(SO_4)_3$ solution. Therefore, no matter what kind of charge the TiO_2 particles carry, the particle surface can selectively absorb positively charged $OH-Al$ species because of the condensation between them. So the TiO_2 particle surface always carries positive charges in coating process.

Therefore, once the $Al_2(SO_4)_3$ solution is titrated into the TiO_2 suspension, the ζ-potential of the TiO_2 particles and the solution pH change, which indicates that the adsorption and condensation of positive $OH-Al$ species on the TiO_2 particles is taking place, and the coating begins.

3. ζ-Potential of the TiO_2 Particles in the Coating Process. The ζ-potential of the TiO_2 particles in the coating process was examined using the ζ-potential analyzer. Samples were taken for ζ-potential measurements every 3 min during the first 15 min of the titration process, every 5 min during the subsequent titration process, and every 20 min during the aging process.
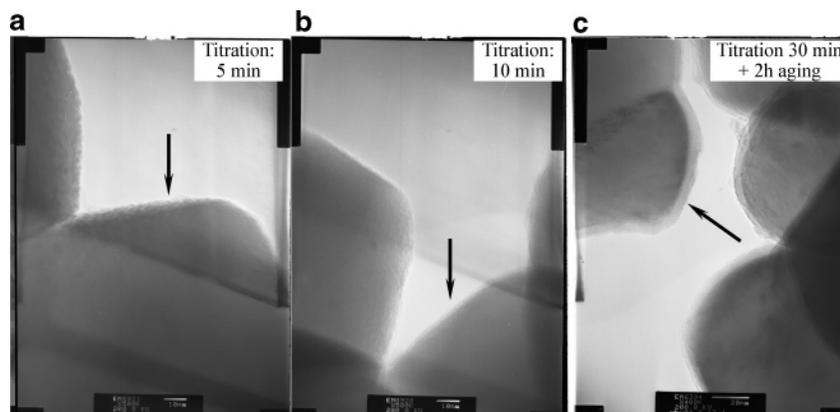
Figure 3. HRTEM images of TiO$_2$ particles during the coating process (pH 4.5, 60) °C. Titration time: (a) 5 min, (b) 10 min, (c) 30 min + 2 h of aging.
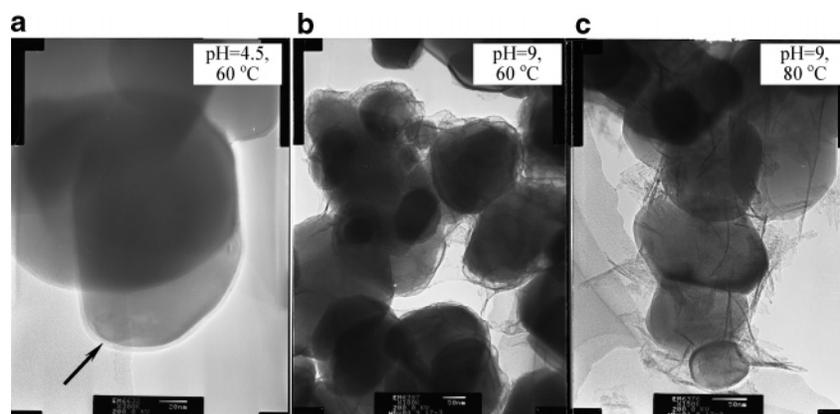
Figure 4. HRTEM images of coated TiO$_2$ particles under different conditions. (a) pH 4.5, 60 °C; (b) pH 9.0, 60 °C; (c) pH 9.0, 80 °C.
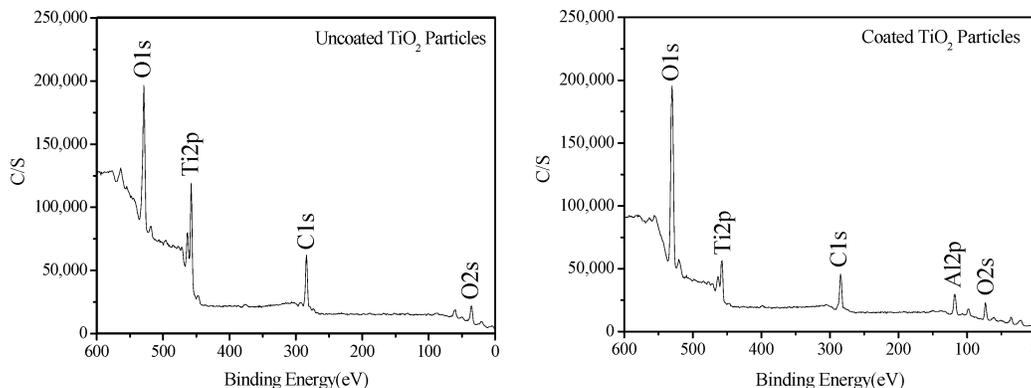
Figure 5. XPS spectra of uncoated and coated TiO$_2$ particles.

The ζ-potential−time curves under different conditions are shown in Figure 2.

Figure 2 shows that the charge carried by the TiO$_2$ particles changed immediately from negative to positive when Al$_2$(SO$_4$)$_3$ solution was titrated, and it was little affected by the ζ-potential of the TiO$_2$ particles at the start, which ranged from about 0 to −30 mV at different pH values. It can be inferred that the positive charge carried by the TiO$_2$ particles resulted from the absorption of OH−Al species. After the titration was completed, the ζ-potential decreased slowly and reached a minimum. Although the ζ-potential values fluctuated during the coating process, the TiO$_2$ particles always carried a positive charge. Therefore, the TiO$_2$ particles and the OH−Al species carried the same sign of charge, and their repulsion of each other dominated the slurry system. The coating depends on the random collision of OH−Al species and TiO$_2$ particles. When the OH−Al species or the particles have enough energy to cross the repulsion threshold, the −OH groups on the TiO$_2$ particles will

condense with the OH−Al species, causing the coating of the OH−Al species on the surface of the TiO$_2$ particles. Our previous work verified through XPS analysis that the Ti−O−Al bond forms at the interface of the TiO$_2$ particles and hydrous Al(OH)$_3$ films, and it can be inferred that the bond results from the condensation of OH−Al species and the −OH groups on TiO$_2$ particles.[18] Because completely inelastic collisions also occur between the OH−Al species, the formation of a small amount of pure particles of hydrated alumina is unavoidable unless the local concentration of the coating agent in the suspension is well controlled.

4. Morphology of Coated TiO$_2$ Particles under Different Conditions. Figure 3 shows the HRTEM images of hydrated alumina coated on the TiO$_2$ particles. Parts a and b of Figure 3 show the images of the TiO$_2$ particles after 5 and 10 min of coating, respectively, Figure 3c shows an image of the TiO$_2$ particles after 30 min of coating and 2 h of aging. Because the coating material was titrated into the suspension by a peristaltic

Table 1. Surface Compositions of Uncoated and Coated Particles from XPS Analysis (atom %)

sample	Ti	Al	O
uncoated	24.03	0.00	75.79
coated	6.98	17.42	75.60

pump continuously during the coating process, the added amount of coating material increased with the coating time, and the coating process proceeded continuously, so the coating layer became increasingly obvious. During the aging period, the unreacted coating materials in the suspension continued to coat the particle surfaces, and the coating layers were self-modified through dissolution and recrystallization. It can be seen in Figure 3c that a layer of amorphous, continuous, and dense hydrous alumina film formed on the TiO_2 particle surface after 30 min of coating and 2 h of aging.

Figure 4 shows HRTEM images of TiO_2 particles coated with hydrous alumina under different coating conditions. Figure 4a shows that a uniform and continuous amorphous hydrous alumina film coating was obtained at pH 4.5 and 60 °C. Figure 4b shows that the morphology of the coating layer was looser at pH 9 and 60 °C. Figure 4c shows that the morphology of the coating layer was no longer continuous and became an elongated fibrillar morphology that looked like fluff at pH 9 and 80 °C.

It can be deduced that the morphology of the coating layer is significantly affected by the hydrolysis rate of Al^{3+}. A high-pH environment accelerates the hydrolysis of Al^{3+} and results in the formation of more multinuclear OH−Al species compared to the situation at low pH, as in Figure 4a, which leads to the OH−Al species getting loosely coated on the surface of the TiO_2 particles, as shown in Figure 4b. The high temperature of 80 °C also accelerates the hydrolysis of Al^{3+} as compared to the conditions in Figure 4b, causing the morphology to become fibrillar, as shown in Figure 4c.

5. Characteristics of Coated TiO_2 Particles. The chemical states of the atoms on the particle surface or in the thin coating layer were examined by XPS.[19,20] The XPS spectra of uncoated and coated TiO_2 particles are shown in Figure 5. Figure 5 shows that both of the spectra contain the Ti 2p and O 1s peaks of TiO_2 particles, as well as C 1s peaks that can be assigned to carbon contamination. Compared to the spectrum of uncoated TiO_2 particles, the spectrum of the coated TiO_2 particles contains Al 2p peaks, which shows that hydrous alumina is coated on the TiO_2 particle surface. Table 1 reports the surface compositions of the samples from the XPS analysis. This shows that there was a high Al concentration on the coated TiO_2 particle surface, that the concentration of Ti clearly decreased, and that the concentration of O remained little changed. Because the penetration depth of the electron beam on the particle surface in XPS is within 10 nm, the atom composition mainly reflects the coated film and the particle surface. The decrease of Ti does not affect the pigmentary properties in the application.

The high-resolution XPS spectra of the O 1s peaks of uncoated and coated TiO_2 particles are shown in Figure 6. These consist of a main peak and a shoulder for both the uncoated and coated particles, although the relative intensities of the two peaks are clearly different. According to the literature[18,21−24] and as shown in Table 2, one peak can be assigned to bulk O^{2-} and the other peak to −OH. Figure 6 shows that the I_{OH}/I_{oxide} ratio of the TiO_2 particle surface changes clearly, from 0.76 to 1.82 after coating, whereas the location of the peaks changes little. The −OH and bulk O^{2-} peaks of the coated TiO_2 particle surface are assigned to $Al(OH)_3$, whereas the −OH and bulk O^{2-} peaks of the uncoated TiO_2 particle surface are assigned to TiO_2, because the coating film of hydrous $Al(OH)_3$ contains
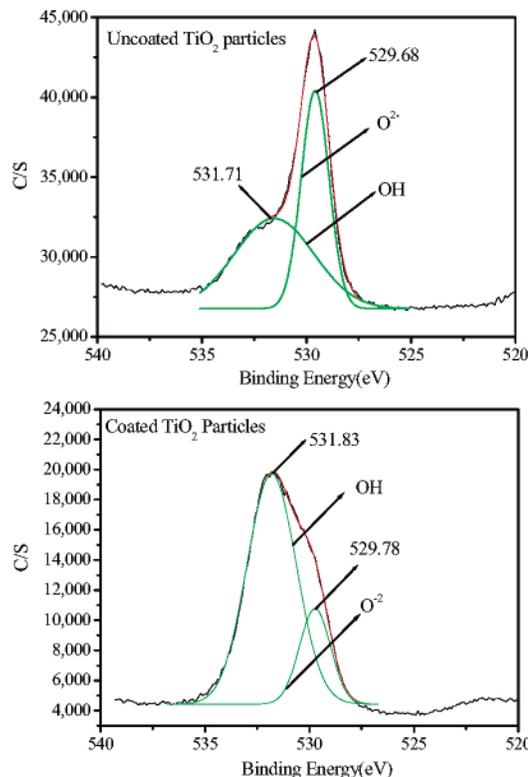
Figure 6. High-resolution XPS spectra of O 1s peaks of uncoated and coated TiO_2 particles.
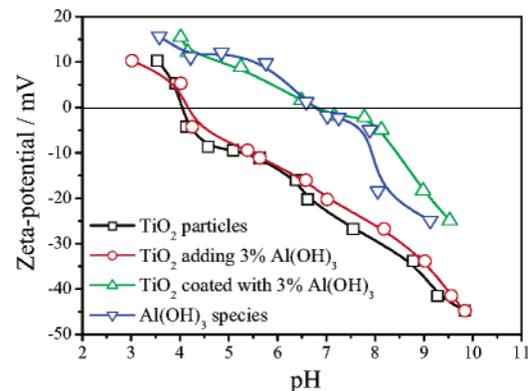
Figure 7. ζ-potentials of uncoated and coated TiO_2 particles.

Table 2. Comparison of the Assignment of the Peaks for OH and Bulk O^{2-} with Literature Values[19]

ref	bulk O^{2-} (eV)	OH	difference (eV)
Sanjines et al.[21]	530.0	531.5	1.5
Mccafferty et al.[22]	530.6	532.4	1.8
Simmons et al.[23]	529.7	531.5	1.8
Riakar et al.[24]	529.5	531.0	1.5
Erdem et al.[19]	530.62	531.86	1.24

much −OH, whereas the surface of the TiO_2 particles mainly contains adsorbed −OH.

Figure 7 shows the electrokinectic behavior of the particles under different conditions. It can be seen that the ζ-potentials of the coated TiO_2 particles were significantly changed. The ζ-potential−pH curve and isoelectric points (IEPs) for the TiO_2 particles coated with hydrous alumina are similar to those of pure $Al(OH)_3$ gel, whereas the TiO_2 particles mixed with 3% $Al(OH)_3$ gel exhibit electrokinectic behavior similar to that of TiO_2 particles. After being coated, the TiO_2 particles have the same surface charge and surface groups as $Al(OH)_3$ gel.

Conclusion

The experimental results reported herein show that the addition of TiO$_2$ particles to an Al$_2$(SO$_4$)$_3$ solution can promote the hydrolysis of Al^{3+} in both acidic and basic solutions. Coating begins with the adsorption of OH−Al species onto the TiO$_2$ particles. The OH−Al species combine with the −OH groups on the TiO$_2$ particle surface, which causes the TiO$_2$ particle surface to carry the same sign of charge as the OH−Al species. The repulsion between the OH−Al species and the TiO$_2$ particles dominates the slurry system. The coating process depends on the random collisions of OH−Al species and TiO$_2$ particles. When the OH−Al species or the particles have enough energy to cross the repulsion threshold, the −OH groups on the TiO$_2$ particles condense with the OH−Al species, leading to the coating of OH−Al species on the surface of the TiO$_2$ particles.

A continuous and uniform dense film coating was obtained under suitable conditions. High-temperature or -pH conditions will accelerate the hydrolysis of Al^{3+}, forming a high concentration of OH−Al species and leading to a loose or discontinuous fibrillar morphology for the coating layer. The TiO$_2$ particles coated with hydrous alumina exhibit electrokinectic behavior similar to that of pure Al(OH)$_3$ gel.

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