

Effects of SO_4^{2-} on the Heterogeneous Precipitation Coating of Hydrous Alumina on TiO_2 Particles in an Aqueous Process

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The effects of foreign inorganic anions on the coating morphologies of TiO_2 particles were experimentally studied by investigating the effects of divalent SO_4^{2-} anions on the precipitation rate, crystallization behavior, and heterogeneous precipitation coating of hydrous alumina. The pH change and critical point of precipitation during base titration into Al^{3+} solutions were investigated. The precipitation rate of OH-Al species was accelerated by an increase in SO_4^{2-} concentration, while the crystallization rate was little changed, so that the crystallization was poor and amorphous gels were preferentially formed. Under the same condition, $\text{Al}(\text{OH})_3$ gels obtained from $\text{Al}_2(\text{SO}_4)_3$ solution or the Al^{3+} solution with added SO_4^{2-} anions were close to amorphous, while the $\text{Al}(\text{OH})_3$ gels from a pure $\text{Al}(\text{NO}_3)_3$ solution were close to crystalline. The conditions conducive for forming amorphous gels were conducive to forming film coating on the core particle surface.

1. Introduction

The preparation of different grades of hydrous alumina is important because they are the precursors for various grades of alumina oxides^{1,2} and coating materials.^{3–5} A layer of alumina oxide coating can increase the $-\text{OH}$ groups on the particle surface, which will improve the dispersibility of the particles in aqueous solution and provide more active sites for organic modification. Furthermore, a layer of continuous film can insulate the particle from contact with the environment, and thus inhibit harmful reactions such as oxidation and decomposition.^{6,7} However, the coating properties greatly depend on the structure and morphology of the coating layer, which determine the electrical, magnetic, mechanical, and diffusive properties.^{8–10} Thus, controlling the morphology of coated particles is very important in industrial application.

Heterogeneous precipitation coating in an aqueous solution has been widely used for particle coating. The coating is usually controlled by adjusting the concentration of the solution complex through changing the experimental parameters, e.g., concentration of coating reagent, pH, and temperature.⁵ There have been many reports on the control of heterogeneous or homogeneous coating through manipulating the supersaturation of the solution complex.^{5,11} In our previous work,¹² the shape and precipitation rate of the OH-Al species were controlled by changing the pH and temperature to alter the structure and morphology of the hydrous alumina coating. Four kinds of typical coating morphologies were observed: dotted coating, film coating, floccule coating, and flake coating. Particle surface properties such as the type and density of $-\text{OH}$ groups play a key role in aqueous heterogeneous coating through their effects on the condensation between the OH-Al species and the $-\text{OH}$ groups on the TiO_2 particle surface and the formation of the film coating.¹³

Besides the experimental parameters (e.g., pH, temperature, concentration of coating materials) and the particle surface properties, other factors such as the presence of foreign anions also affect the nucleation and growth of coating layer, and have been used to control the crystal structure, size, and morphology.^{14–16}

It was reported that the precipitation of hydroxide alumina was affected by the presence of foreign organic anions,¹⁷ which adsorbed on the particle surface and blocked crystal growth.

In this paper, the effects of the inorganic anion SO_4^{2-} on the precipitation rate of OH-Al species and the crystal structure, as well as the controlling of the hydrous alumina coating morphology on a TiO_2 particle surface, were investigated.

2. Experimental Section

2.1. Reagents. Commercial TiO_2 particles from the sulfate process were used. These had the rutile structure, were 200 nm in mean diameter, were nonporous, and had a surface area of 6.54 m^2/g . Other chemicals used in the experiments were analytical reagent (AR) grade.

2.2. Preparation of $\text{Al}(\text{OH})_3$ Gel. A 1 mol/L NaOH solution was titrated into 100 mL of 0.3 mol/L $\text{Al}_2(\text{SO}_4)_3$ solution, $\text{Al}(\text{NO}_3)_3$ solution, or a mixture of $\text{Al}(\text{NO}_3)_3$ and Na_2SO_4 solutions, respectively. After 2 h aging, the $\text{Al}(\text{OH})_3$ gel was filtered and washed repeatedly until SO_4^{2-} was no longer detected using a BaCl_2 solution. The cake was dried at 30 °C under vacuum for 20 h, followed by grinding into dispersed particles for characterization.

2.3. Base Titration. Twenty milliliters of 0.1 mol/L NaOH solution was titrated into 500 mL of 0.001 mol/L $\text{Al}(\text{NO}_3)_3$ solution, or a mixture of $\text{Al}(\text{NO}_3)_3$ and different concentrations of Na_2SO_4 solution, respectively, by a peristaltic pump. The titration speed was 0.5 mL/min. The total moles of NaOH molecules was 4 times that of Al^{3+} ions. As the NaOH solution was titrated, in the initial stage, there was no precipitant until a critical point was reached, where the precipitant of hydrous alumina formed. After that, the hydrous alumina was formed gradually with the titration. A particle sizer (MasterSizer, MICRO-PLUS, Malvern Instruments, England) was used to measure the obstruction of the solution online, which reflects the concentration of the precipitated particles. The pH and the obstruction change with the titrated amount of NaOH solution were recorded.

2.4. Particle Coating Process. The experiments were carried out in a flask with the temperature and pH measured online. The TiO_2 particles, at a concentration of 50 g/L, were dispersed in deionized water by continuous ultrasonic treatment for 30 min before the coating titration. Then, 0.6 mol/L Al^{3+} ion

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solution (0.3 mol/L $\text{Al}_2(\text{SO}_4)_3$ solution, 0.6 mol/L $\text{Al}(\text{NO}_3)_3$ solution, or a mixture of 0.6 mol/L $\text{Al}(\text{NO}_3)_3$ and Na_2SO_4 solutions of different concentrations) and 1 mol/L NaOH solution were titrated into the TiO_2 suspension simultaneously. The TiO_2 suspension was vigorously stirred and adjusted to a set pH by controlling the titrating speed of the NaOH solution with the titrating speed of the Al^{3+} ion solution kept constant. The reaction temperature was controlled at a set value by a constant-temperature bath. After titration, the suspension was aged for 1 h with stirring. Then, the coated TiO_2 particles were filtered and washed repeatedly until SO_4^{2-} was no longer detected using a BaCl_2 solution. The cakes were dried at 120 °C for 12 h and then subsequently ground into dispersed particles for characterization.

Many factors affect the coating morphology, e.g., pH, temperature, coating reagent concentration, particle concentration, particle surface properties, feeding order, and agitation strength. The experimental conditions were very carefully controlled to ensure the reproducibility of the results.

2.5. Characterization. The film structure was characterized by X-ray diffraction (XRD; Rigaku2500, Rigaku, Japan) using $\text{Cu K}\alpha$ radiation with $\lambda = 1.5418 \text{ \AA}$ in $\theta-2\theta$ scan mode. The morphology and structure of the hydrous alumina coating film on the particle surface were examined by high-resolution transmission electron microscopy (HRTEM; JEM-2011, JEOL Co., Japan). The critical point of precipitation was detected by a particle sizer (MasterSizer, MICRO-PLUS, Malvern Instruments, England) with a He-Ne laser at 633 nm wavelength.

3. Results and Discussion

The main interactions in the suspension are the van der Waals attractive force (the dominant force in particle-particle attraction) between particles and the Coulombic repulsive force from similarly charged particles. The van der Waals force mainly depends on the intrinsic nature of both the particles and the solvent, and is not easily manipulated for a specified system. The electrostatic force between particles can be changed by adjusting the pH toward or away from the isoelectric point, or by changing the ionic strength of the suspension to alter the thickness of the double layer.¹⁸ It has been shown that coating begins with the adsorption of $\text{OH}-\text{Al}$ species onto the TiO_2 particle surface.¹⁹ The $\text{OH}-\text{Al}$ species combine with the $-\text{OH}$ groups on the TiO_2 particle surface, which cause the TiO_2 particle surface to carry the same sign of charge as the $\text{OH}-\text{Al}$ species. In recognition of this, the divalent SO_4^{2-} anions were introduced to manipulate the precipitation rate and crystal structure of the hydrous alumina through changing the ionic strength in the suspension and Coulombic repulsive interaction between the particles.

3.1. Effect of SO_4^{2-} Anion on Precipitation Rate. NaOH was titrated into a Al^{3+} solution, and the pH and obstruction changes with $\text{OH}^-/\text{Al}^{3+}$ ratio (mol/mol) are shown in Figure 1. Figure 1a shows the situation of NaOH titration into the $\text{Al}(\text{NO}_3)_3$ solution, and Figure 1b shows NaOH titration into the mixed solution of $\text{Al}(\text{NO}_3)_3$ and Na_2SO_4 . The obstruction value reflects the particle concentration in the aqueous solution, and the critical point of particle formation can be detected.

As shown in Figure 1a, in the initial stage of the titration of the NaOH solution, the two curves of pH and obstruction were both hardly changed, and the obstruction was almost zero, which indicates that there was no precipitant or particle formed in the aqueous solution. All the OH^- from NaOH titration in the aqueous solution was neutralized by H^+ released from the hydrolysis of Al^{3+} ions. When the mole ratio of $\text{OH}^-/\text{Al}^{3+}$

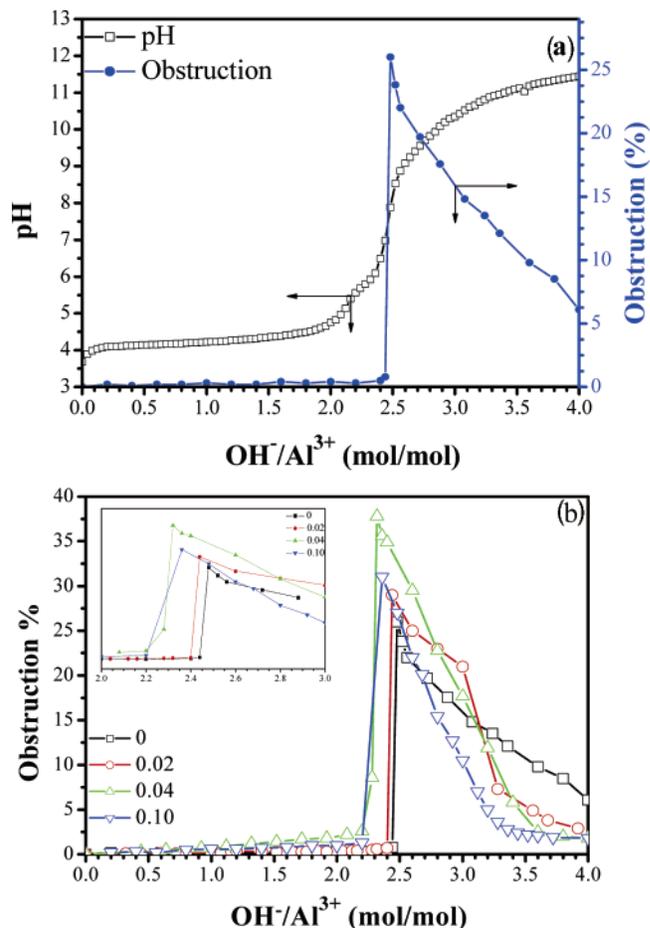


Figure 1. NaOH titration into Al^{3+} solution. (a) pH and obstruction vs $\text{OH}^-/\text{Al}^{3+}$ (NaOH titration into $\text{Al}(\text{NO}_3)_3$ solution). (b) Obstruction vs $\text{OH}^-/\text{Al}^{3+}$ (NaOH titration into $\text{Al}(\text{NO}_3)_3$ and Na_2SO_4 mixture). $\text{SO}_4^{2-}/\text{Al}^{3+}$ (mol/mol): \square , 0; \circ , 0.02; \triangle , 0.04; ∇ , 0.10.

approached 2.5, the slope of the two curves increased sharply, and the obstruction value increased abruptly, which indicated that a large amount of precipitant or particles was formed, and the effect of the added NaOH solution was mainly to raise the aqueous pH. After that the pH increased very slowly, and the obstruction decreased gradually, which implied that the OH^- from NaOH titration was mainly consumed in dissolving the $\text{Al}(\text{OH})_3$ gels. As the mole ratio of $\text{OH}^-/\text{Al}^{3+}$ got close to 3.0, the $\text{Al}(\text{OH})_3$ gels were dissolved as soon as they formed, which implied that the newly formed $\text{Al}(\text{OH})_3$ gels were active and not stable.

The inflection point of obstruction indicated the critical point where precipitation started in the aqueous solution. Comparing the curves in Figure 1b, it was found that the mole ratios of $\text{OH}^-/\text{Al}^{3+}$ at the precipitation starting point decreased with the increase of the $\text{SO}_4^{2-}/\text{Al}^{3+}$ ratios; they were 2.45, 2.41, 2.22, and 2.21 at the $\text{SO}_4^{2-}/\text{Al}^{3+}$ mole ratios of 0, 0.02, 0.04, and 0.10, respectively. This indicated that the introduction of SO_4^{2-} anions accelerated the precipitation rate of the $\text{OH}-\text{Al}$ species, and the effects at a high concentration of SO_4^{2-} were more obvious. When the mole ratio of $\text{SO}_4^{2-}/\text{Al}^{3+}$ reached 0.04, the change in the critical point of precipitation was small.

3.2. Effect of SO_4^{2-} Anion on the $\text{Al}(\text{OH})_3$ Gel Structure. The effects of SO_4^{2-} anions on $\text{Al}(\text{OH})_3$ gel structure were investigated and are shown in Figures 2 and 3. Parts a and b of Figure 2 show the X-ray diffraction spectra of the $\text{Al}(\text{OH})_3$ gels obtained from NaOH titration into $\text{Al}(\text{NO}_3)_3$ and $\text{Al}_2(\text{SO}_4)_3$ solutions, respectively, at 30, 60, and 85 °C.

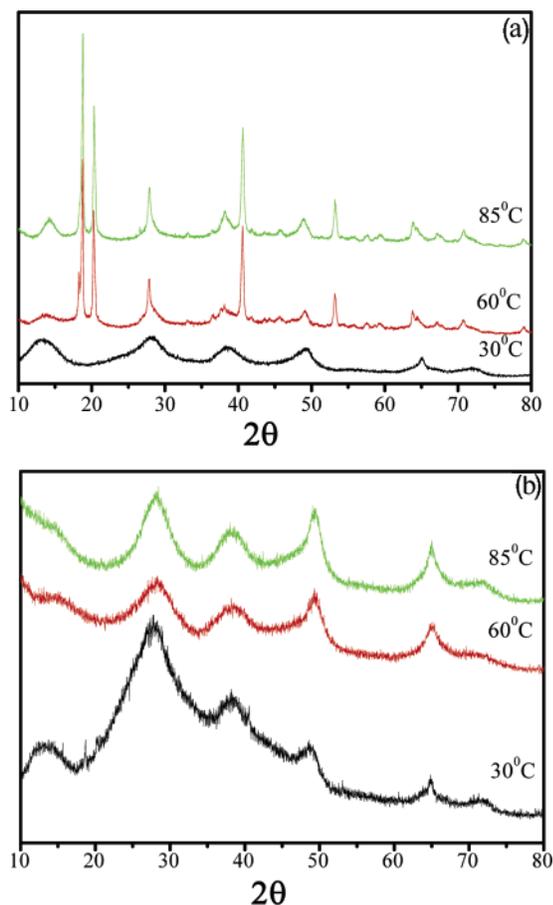


Figure 2. X-ray diffraction pattern of Al(OH)₃ gel. (a) NaOH titration into Al(NO₃)₃ solution; (b) NaOH titration into Al₂(SO₄)₃ solution.

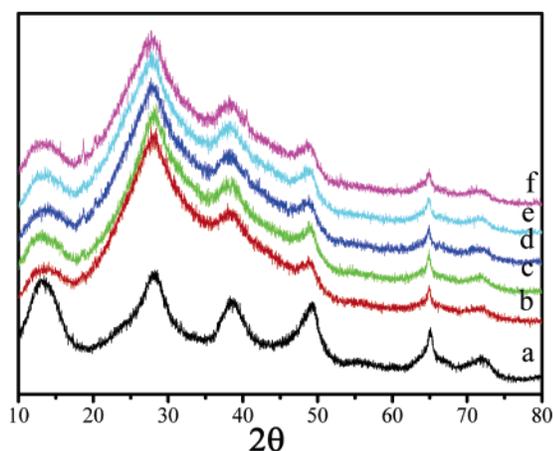


Figure 3. X-ray diffraction pattern of Al(OH)₃ gel. NaOH titration into Al(NO₃)₃ solution (SO₄²⁻/Al³⁺, mol/mol): (a) 0; (b) 0.05; (c) 0.10; (d) 0.50; (e) 1.00. NaOH titration into Al₂(SO₄)₃ solution: (f).

In the case of NaOH titration into the Al(NO₃)₃ solution, the spectra of the Al(OH)₃ gels changed from poorly crystallized gel of pseudoboehmite to a highly crystallized gel of a mixture of pseudoboehmite and bayerite with the increase in reaction temperature, as shown in Figure 2a. In the case of NaOH titration into the Al₂(SO₄)₃ solution, the spectra of the Al(OH)₃ gels changed from amorphous to pseudoboehmite with the increase in reaction temperature, as shown in Figure 2b. The two control titrations were performed with the same concentration of NaOH and Al³⁺ and titrating speed of NaOH solution.

For the gels from the same Al³⁺ solution, at the lower temperature, poorly crystallized Al(OH)₃ gels formed, and the

crystal structures were pseudoboehmite or amorphous. At the higher temperature, highly crystallized Al(OH)₃ gels formed. At the same reaction temperature, the Al(OH)₃ gels from the NaOH titration into the Al(NO₃)₃ solution were more crystallized than that into the Al₂(SO₄)₃ solution, as can be seen by comparing Figure 2a and Figure 2b. This indicates that SO₄²⁻ and NO₃⁻ cause differing crystallization of the Al(OH)₃ gels.

Figure 3 shows the X-ray diffraction spectra of the Al(OH)₃ gels prepared with different SO₄²⁻/Al³⁺ ratios in the Al(NO₃)₃ solution. This shows that when SO₄²⁻ anions were introduced into the aqueous solution, the gel structure changed from poorly crystallized (SO₄²⁻/Al³⁺ = 0) to amorphous with broad peaks (SO₄²⁻/Al³⁺ ≥ 0.05), which indicated that the presence of SO₄²⁻ brings about lower crystallized gels, like the effect of a lower temperature. When the SO₄²⁻/Al³⁺ ≥ 0.05, the gel structure changed little. When NO₃⁻ anions were introduced into the aqueous solution, the amorphous gels formed from the Al₂(SO₄)₃ solution did not change, which shows that NO₃⁻ had little effect on Al(OH)₃ gel formation. The divalent SO₄²⁻ anions affect the crystallization behavior of Al(OH)₃ gels more than the monovalent NO₃⁻.

3.3. Effect of SO₄²⁻ Anion on the Coating Process. TiO₂ particle coating was carried out using Al(NO₃)₃ solutions as the coating reagent at pH 9 and temperatures of 0, 30, and 70 °C, respectively. All other conditions were the same as in our previous work.¹² The HRTEM photos of the coated TiO₂ particles are shown in Figure 4. This shows that the morphologies under the three conditions are floccule coating, flake coating, and flake coating, respectively. However, according to the coating morphology “phase diagram” we published last year,¹² the morphologies should be film coating, floccule coating, and flake coating under these conditions, with Al₂(SO₄)₃ solution as the coating reagent. This indicated that SO₄²⁻ and NO₃⁻ have different effects on the coating morphology of hydrous alumina.

TiO₂ particle coating with different coating reagents, i.e., Al₂(SO₄)₃ solution, Al(NO₃)₃ solution, and a mixture of Al(NO₃)₃ and Na₂SO₄ solutions, respectively, was carried out at pH 6 and 32 °C. The HRTEM photos of the coated particles are shown in Figure 5. According to the coating morphology “phase diagram”,¹² they should all be film coating, while Figure 5 shows film coating, floccule coating, and film coating, respectively, and the coatings from Al₂(SO₄)₃ solution were easier to form film than those from Al(NO₃)₃ solution. The morphologies of the coated particles obtained from the mixture of Al(NO₃)₃ and Na₂SO₄ solutions, as shown in Figure 5c, were close to film coating under the same condition, although the films were not as continuous and uniform as that in Figure 5a. This shows that SO₄²⁻ anions help to form film coating under the same condition, and the coating “morphology phase diagram” is affected by different anions. Therefore, anions play an important role in determining the coating morphology, which was not taken into account previously.

3.4. Mechanism of the SO₄²⁻ Anion Effect. The SO₄²⁻ anions have two effects on the hydrous alumina crystallization. One is through affecting the particle–particle interactions. When SO₄²⁻ anions were introduced, the ionic strength in the aqueous phase was increased and the electrical double layer of the particles was compressed,²⁰ so that the Coulombic repulsive interaction between OH–Al species was decreased. This led to a higher collision probability between the OH–Al species, which increased the precipitation rate, and the OH⁻/Al³⁺ ratio for precipitation decreased with the increase of SO₄²⁻/Al³⁺ ratio, as shown in Figure 1b. As compared with the increase of

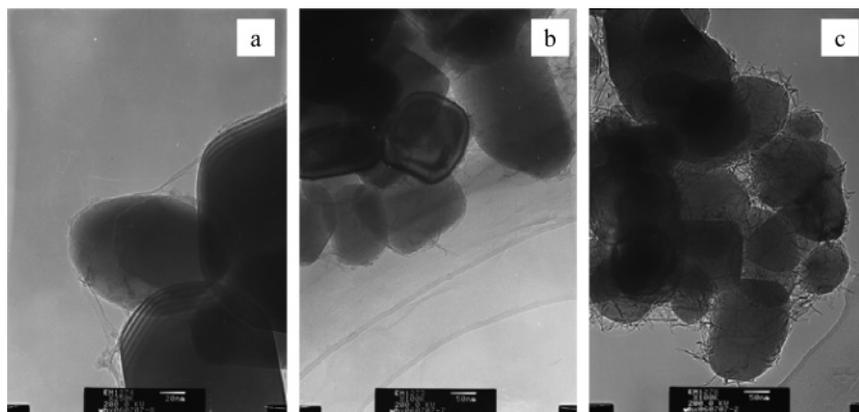


Figure 4. HRTEM images of coated TiO₂ particles from the precipitation of Al(NO₃)₃, pH 9: (a) 0 °C; (b) 30 °C; (c) 70 °C.

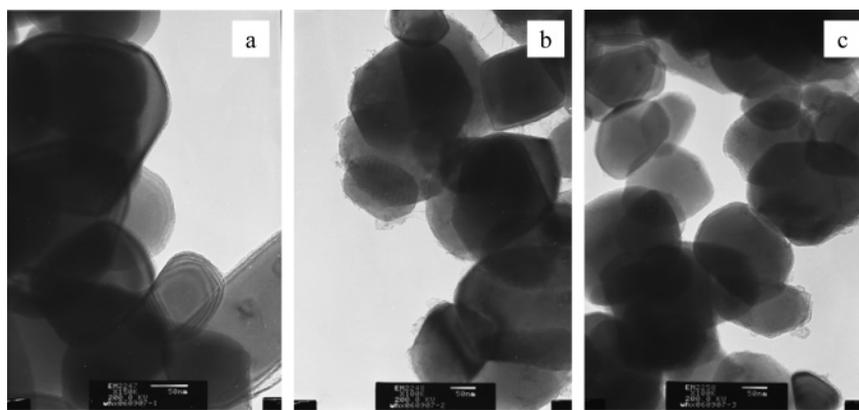


Figure 5. HRTEM images of coated TiO₂ particles. (a) NaOH titration into Al₂(SO₄)₃ solution; (b) NaOH titration into Al(NO₃)₃ solution; (c) NaOH titration into Al(NO₃)₃ solution in the presence of Na₂SO₄.

precipitation rate, the crystal growth rate was little changed, so the crystallization was limited, resulting in an amorphous gel as shown in Figure 3.

Compared with monovalent ions, divalent and trivalent ions with the same quantity charge can increase the ionic strength and compress the double layer more because the ionic strength has a direct proportion to ion number and the square of valence. The Coulombic repulsive interaction, precipitation rate, and precipitate structure of the hydrous alumina will be affected. The obstruction vs OH⁻/Al³⁺ ratio during the NaOH titration into the Al(NO₃)₃ solution with different anions is shown in Figure 6. This shows that the divalent anions SO₄²⁻ and SiO₃²⁻ affect the critical point of precipitation more significantly than the monovalent anion Cl⁻. Although NaH₂PO₄ has the trivalent PO₄³⁻ ion, it normally presents as H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻, and Na₂SiO₃ was hydrolyzed into many kinds of different valent ions in the aqueous solution, so the same amount of NaH₂PO₄ and Na₂SiO₃ did not affect the critical point of precipitation as much as Na₂SO₄.

The other effect of the SO₄²⁻ anions is that of playing a bridge in precipitation. It was reported that the adsorption of surface-active species affects the crystallization rate and mechanism.²¹ In this case, SO₄²⁻ anions may adsorb on and complex with the OH–Al species. The XPS spectra of the coated TiO₂ particles shown in Figure 7 show a weak peak that indicates the presence of elemental S. This is consistent with adsorption or complex formation between SO₄²⁻ and OH–Al species, in which the SO₄²⁻ played a role as a bridge. After the condensation between OH–Al species and –OH on the particle surface, the SO₄²⁻ may remain. After absorption, the interface is changed, resulting in an alteration of the crystallization process. In our experiment, EDTA solution was also explored as an

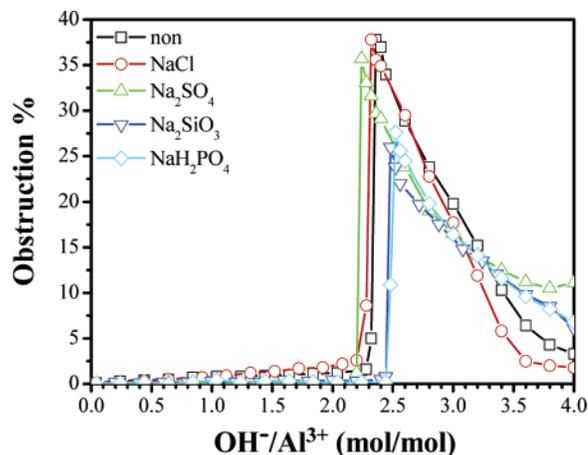


Figure 6. Obstruction vs OH⁻/Al³⁺ during NaOH titration into Al(NO₃)₃ (mol/mol): □, no foreign salt; ○, NaCl/Al(NO₃)₃ = 0.04; △, Na₂SO₄/Al(NO₃)₃ = 0.04; ▽, Na₂SiO₃/Al(NO₃)₃ = 0.04; ◇, NaH₂PO₄/Al(NO₃)₃ = 0.04.

additive, and it was found that homogeneous precipitation occurred, so strong chelation is not helpful for heterogeneous precipitation.

In the coating process, the introduction of SO₄²⁻ anions can also increase the ionic strength, compress the electrical double layer, decrease the Coulombic repulsive interactions, and increase the collision probability between the core particle surface and the OH–Al species, so that the precipitation rate of OH–Al species was increased and an amorphous hydrous alumina coating was preferred. When there is a more disordered structure of the hydrous alumina coated on the TiO₂ particle surface, the particle surface is rougher, and there is more OH–

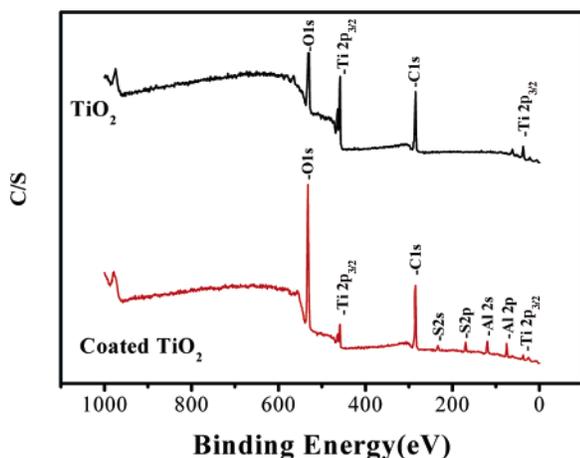


Figure 7. XPS spectra of uncoated and coated TiO_2 particles.

Al species sticking to the rougher surface. In an extreme case, all the surface sites are available for nucleation and crystallization, and a film coating is more easily obtained than when only discrete sites are available on the particle surface.

From the analysis of the structure of the hydrous alumina gels and the corresponding coating results, it was found that a film coating is likely to form when the conditions favor forming amorphous gels. The introduction of SO_4^{2-} anions facilitates the formation of amorphous hydrous alumina.

4. Conclusion

The effects of the presence of SO_4^{2-} on heterogeneous precipitation coating in an aqueous process were studied. The introduction of SO_4^{2-} distinctly increased the precipitation rate in $\text{Al}(\text{OH})_3$ gel formation, and the $\text{Al}(\text{OH})_3$ gel formed was amorphous or poorly crystallized. Film coating of the TiO_2 particles was easily achieved with the conditions where the $\text{Al}(\text{OH})_3$ gel formed was amorphous.

The introduction of SO_4^{2-} anions increased the ionic strength and compressed the thickness of the double layer, which decreased the repulsive interactions between the core particle surface and OH–Al species, and increased the collision possibility and the precipitation rate. Both divalent and trivalent ions can accelerate the precipitation rate. The high precipitation rate favored an amorphous structure for the hydrous alumina gel and coating film. The amorphous structure provides more sites for nucleation and condensation compared with a well-crystallized structure. The SO_4^{2-} anion plays a role as a bridge for OH–Al species coating. Some SO_4^{2-} anions may remain in the film.

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