Research Article

Synthesis of $\text{Al}(\text{OH})_3$ Nanostructures from $\text{Al}(\text{OH})_3$ Microagglomerates via Dissolution-Precipitation Route

Bo Yu,¹ Zhenhao Tian,¹ Jie Xiong,² and Lan Xiang¹

¹ Department of Chemical Engineering, Tsinghua University, Beijing 10084, China

² Department of Chemical Engineering, China University of Petroleum, Beijing 102249, China

Correspondence should be addressed to Lan Xiang; xianglan@mail.tsinghua.edu.cn

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A facile method was developed to synthesize $\text{Al}(\text{OH})_3$ nanostructures from $\text{Al}(\text{OH})_3$ microagglomerates by dissolution in $9.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH at 115°C followed by dilution and aging of the solution at room temperature. The influence of $\text{Al}(\text{OH})_3$ nanoseed and surfactants as sodium dodecyl sulfate (SDS), polyethylene glycol 6000 (PEG6000), and cetyltrimethylammonium bromide (CTAB) on the formation of the $\text{Al}(\text{OH})_3$ nano-structures was investigated. The experimental results indicated that the $\text{Al}(\text{OH})_3$ microspheres composed of nanoparticles were prepared in the blank experiment, while dispersive $\text{Al}(\text{OH})_3$ nano-particles with a diameter of 80–100 nm were produced in the presence of $\text{Al}(\text{OH})_3$ nano-seed and CTAB.

1. Introduction

The synthesis of $\text{Al}(\text{OH})_3$ nanostructures has been paid much attention in recent years owing to their unique properties and wide applications in plastics, rubbers, papers, glasses and medicines, and so forth [1–4]. $\text{Al}(\text{OH})_3$ microparticles were usually produced in the aluminum metallurgical factories via the Bayer route, which included the leaching of the bauxite ores at alkaline hydrothermal condition ($150\text{--}250^\circ\text{C}$), the removing of impurities as Si and Fe at elevated temperatures, and the precipitation of the $\text{Al}(\text{OH})_3$ microparticles in the presence of $\text{Al}(\text{OH})_3$ seed by gradually cooling of the sodium aluminate solution from $90\text{--}100^\circ\text{C}$ to $50\text{--}60^\circ\text{C}$ which usually lasted 48–72 h [5–8]. Many wet chemical methods have been developed to synthesize the $\text{Al}(\text{OH})_3$ nanostructures. For example, Li et al. [9] produced the $\text{Al}(\text{OH})_3$ nanowhiskers with a length of 8–12 μm and a diameter of 100 nm by dropping $0.05 \text{ mol}\cdot\text{L}^{-1}$ HCl to $1.6 \text{ mol}\cdot\text{L}^{-1}$ sodium aluminate at 60°C . Chen et al. [10] synthesized the $\text{Al}(\text{OH})_3$ hexagonal plates with a diameter of 100–200 nm and a thickness of 20–30 nm by carbonation of the sodium aluminate solution at room temperature. Li et al. [11] produced the $\text{Al}(\text{OH})_3$ nanoparticles with an average size of 30–40 nm from the dilute sodium aluminate solution containing $0.4 \text{ mol}\cdot\text{L}^{-1}$

NaOH in the presence of $\alpha\text{-Al}_2\text{O}_3$ nanoseed and polyethylene glycol 20000 (PEG20000). However, some problems still existed in the former methods, such as low efficiency in the dilute system, the use of the expensive organic solvents, and the discharge of waste water or byproducts. Wang et al. synthesized $\text{Al}(\text{OH})_3$ particles with an average diameters of 0.5–1.2 μm by dissolution of the agglomerated $\text{Al}(\text{OH})_3$ microagglomerates with an average diameter of 1.5 μm in $2.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution at $90\text{--}100^\circ\text{C}$ and then cooled down to $50\text{--}70^\circ\text{C}$. Up to now, it is still a challenge to develop a moderate, efficient, and environmentally friendly method for the synthesis of $\text{Al}(\text{OH})_3$ nanostructures.

Herein, a facile dissolution precipitation method was developed in this paper to synthesize $\text{Al}(\text{OH})_3$ nanostructures from $\text{Al}(\text{OH})_3$ microagglomerates. The influences of the $\text{Al}(\text{OH})_3$ nanoseed and the surfactants including SDS, PEG6000, and CTAB on the formation of $\text{Al}(\text{OH})_3$ nanostructures were discussed.

2. Experimental

2.1. Experimental Procedure. Figure 1 shows the morphology and the thermogravimetric analysis of the raw material and the $\text{Al}(\text{OH})_3$ seed. $\text{Al}(\text{OH})_3$ raw material was Provided by

FIGURE 1: TG curve and morphology of $\text{Al}(\text{OH})_3$ raw material (a) and seed (b).

an aluminum metallurgical factory in Shandong province, China. $\text{Al}(\text{OH})_3$ seed was synthesized by coprecipitation of $0.5 \text{ mol}\cdot\text{L}^{-1}$ $\text{Al}(\text{NO}_3)_3$ and $1.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH at room temperature, keeping the initial molar ratio of $\text{Al}(\text{NO}_3)_3$ to NaOH at 1 : 3. As shown in Figure 1(a), $\text{Al}(\text{OH})_3$ raw material was composed mainly of the irregular agglomerates with a diameter of 5–20 µm, and the weight loss (36.11%) occurred between 30 and 800°C should be attributed to the removal of the crystal water; thus, the formula for the raw material was deduced as $\text{Al}_2\text{O}_3\cdot 3.20\text{H}_2\text{O}$. The data in Figure 1(b) showed that the particle size of the $\text{Al}(\text{OH})_3$ seed was 20–40 nm and the weight loss between 30 and 800°C was 35.04%, and then the formula for the seed was deduced as $\text{Al}_2\text{O}_3\cdot 3.15\text{H}_2\text{O}$.

Figure 2 shows the flow chart for the formation of the $\text{Al}(\text{OH})_3$ nanostructures from the $\text{Al}(\text{OH})_3$ microagglomerates.

Dissolution of $\text{Al}(\text{OH})_3$ in NaOH solution. 66.4 g of $\text{Al}(\text{OH})_3$ raw material was dissolved in 110 mL of 3.0–11.0 $\text{mol}\cdot\text{L}^{-1}$ NaOH at 115°C for 0.5 h to prepare the sodium aluminum solution with or without the existence of the un-dissolved $\text{Al}(\text{OH})_3$. The solutions or the supernatants were used to analyze the dissolution of $\text{Al}(\text{OH})_3$.

FIGURE 2: Flow chart for the formation of nano- $\text{Al}(\text{OH})_3$ from $\text{Al}(\text{OH})_3$ microagglomerates.

FIGURE 3: Dissolution of $\text{Al}(\text{OH})_3$ microagglomerates in NaOH solution.

Formation of $\text{Al}(\text{OH})_3$ nanostructures. 66.4 g of $\text{Al}(\text{OH})_3$ raw material was dissolved in 110 mL of $9.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH at 115°C for 0.5 h to get the sodium aluminum solution. The solution was then cooled down to room temperature and diluted with deionized water to get a solution containing $3.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH . Then, a certain amount of the $\text{Al}(\text{OH})_3$ nanoseed and surfactant (SDS, EDTA, or PEG 6000) were added to the diluted sodium aluminum solution to produce a solution containing $0.125 \text{ mol}\cdot\text{L}^{-1}$ $\text{Al}(\text{OH})_3$ nanoseed and $13.0 \text{ g}\cdot\text{L}^{-1}$ surfactant. The sodium aluminum solution was aged for 0–10.0 h to fabricate the $\text{Al}(\text{OH})_3$ precipitate. Then, the $\text{Al}(\text{OH})_3$ precipitate was washed by deionized water and

FIGURE 4: Morphology of $\text{Al}(\text{OH})_3$ formed in the absence (a–c) and presence (d–f) of seed. Aging time (h): a, c—2.0; b, d—6.0; and c, f—10.0.

ethanol and dried at 105°C for 4.0 h. All of the chemical reagents used in the experiments were analytical grade without further purification.

2.2. Analysis. The morphology of the samples was examined by the field emission scanning electron microscopy (FESEM, JSM 7401F, JEOL, Japan). The structures of the samples were identified by the X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) patterns using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ nm}$). The composition of the samples was identified by the thermogravimetric analyzer (TG/DSC, Mettler Toledo, Switzerland). The concentration of the soluble Al ion was analyzed by the EDTA complex- Zn^{2+} titration method [12].

3. Results and Discussions

3.1. Dissolution of $\text{Al}(\text{OH})_3$ Microagglomerates in NaOH Solution. Figure 3 shows the dissolution of the $\text{Al}(\text{OH})_3$ microagglomerates in $3.0\text{--}11.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH solutions. In the experimental conditions, the increase of NaOH concentration from $3.0 \text{ mol}\cdot\text{L}^{-1}$ to $11.0 \text{ mol}\cdot\text{L}^{-1}$ favored the dissolution of $\text{Al}(\text{OH})_3$. It was found that the raw material was dissolved completely if $[\text{NaOH}] \geq 9.0 \text{ mol}\cdot\text{L}^{-1}$. Therefore, $9.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH was adapted to dissolve the $\text{Al}(\text{OH})_3$ raw material in the later experiments.

3.2. Precipitation of $\text{Al}(\text{OH})_3$ at Room Temperature

3.2.1. Influence of $\text{Al}(\text{OH})_3$ Nanoseed. Figure 4 shows the morphology of the $\text{Al}(\text{OH})_3$ nanostructures formed in the absence and presence of $\text{Al}(\text{OH})_3$ nanoseed. As shown in Figures 4(a)–4(c), agglomerated microspheres were prepared in the blank experiment. The microspheres were composed of the plates with a diameter of $0.6\text{--}1.0 \mu\text{m}$ and a thickness of

$0.2\text{--}0.3 \mu\text{m}$, and the plates were made up of the nanoparticles with a diameter of $80\text{--}100 \text{ nm}$. The diameters of the microspheres formed at 2.0 h, 6.0 h, and 10.0 h were $0.5\text{--}1.5 \mu\text{m}$, $1.0\text{--}3.5 \mu\text{m}$, and $1.0\text{--}4.0 \mu\text{m}$, respectively, revealing that the sizes of the microspheres increased with the increase of the aging time. Dispersive $\text{Al}(\text{OH})_3$ nanoplates with a diameter of $250\text{--}350 \text{ nm}$ and a thickness of 100 nm were produced in the presence of $0.125 \text{ mol}\cdot\text{L}^{-1}$ $\text{Al}(\text{OH})_3$ nanoseed, and the morphology of the nanoplates formed at 2.0 h, 6.0 h, and 10.0 h were quite similar to each other.

Figure 5 shows the TG curves and the XRD patterns of the $\text{Al}(\text{OH})_3$ nanoplates formed in the presence of $\text{Al}(\text{OH})_3$ nanoseed. As shown in Figure 5(a), a weight loss of 35.91% occurred in the temperature range of $30\text{--}800^\circ\text{C}$; thus, the formula of the $\text{Al}(\text{OH})_3$ nanoplates was deduced as $\text{Al}_2\text{O}_3\cdot 3.17\text{H}_2\text{O}$. The phenomenon that the number of water molecular was slightly higher than 3.0 revealed that some water was absorbed physically by the $\text{Al}(\text{OH})_3$ nanoplates. Most of the diffraction peaks in Figure 6(b) can be indexed as gibbsite (PDF no. 74-1775, $a = 8.676 \text{ \AA}$, $b = 5.070 \text{ \AA}$, and $c = 9.721 \text{ \AA}$), and the peak at $2\theta = 40.506^\circ$ revealed that a minor amount of bayerite (PDF no. 20-0011, $a = 5.062 \text{ \AA}$, $b = 8.671 \text{ \AA}$, and $c = 4.713 \text{ \AA}$) also existed in the $\text{Al}(\text{OH})_3$ nanoplates.

Figure 6 shows the influence of $\text{Al}(\text{OH})_3$ nanoseed on the precipitation of $\text{Al}(\text{OH})_3$ nanostructures. The precipitation of $\text{Al}(\text{OH})_3$ was accelerated by the addition of $\text{Al}(\text{OH})_3$ nanoseed obviously. 63.0% of the soluble Al ion in the sodium aluminate solution was converted to the $\text{Al}(\text{OH})_3$ precipitate after aging for 2.0 h, while only about 1.0% of the soluble Al ion was precipitated after aging for 2.0 h in the blank experiment.

The influence of $\text{Al}(\text{OH})_3$ nanoseed on the morphology and the precipitation of the $\text{Al}(\text{OH})_3$ nanostructures may be

FIGURE 5: TG curve (a) and XRD spectrum (b) of $\text{Al}(\text{OH})_3$ nanoplates formed in the presence of $\text{Al}(\text{OH})_3$ nanoseed. ●—Gibbsite- $\text{Al}(\text{OH})_3$, Δ—Bayerite- $\text{Al}(\text{OH})_3$.

FIGURE 6: Precipitation of $\text{Al}(\text{OH})_3$ in the absence (a) and presence (b) of $\text{Al}(\text{OH})_3$ nanoseed.

explained as follows. In the absence of $\text{Al}(\text{OH})_3$ nanoseed, $\text{Al}(\text{OH})_3$ was first precipitated homogeneously and slowly from the sodium aluminate solution, and the $\text{Al}(\text{OH})_3$ fine particles formed at the early aging stage acted as the nucleus for the subsequent precipitation of $\text{Al}(\text{OH})_3$, leading to the gradual growth of the agglomerated microspheres. Meanwhile, in the presence of $\text{Al}(\text{OH})_3$ nanoseed, many $\text{Al}(\text{OH})_3$ nanoparticles were added to the initial sodium aluminate solution, and they acted as the nucleus for the later heterogeneous precipitation of $\text{Al}(\text{OH})_3$ from the sodium aluminate solution, leading to the fast conversion of most of the soluble Al ion to $\text{Al}(\text{OH})_3$ within 2.0 h of aging and producing $\text{Al}(\text{OH})_3$ nanoplates with quite similar shapes.

3.3. Influence of Surfactants. The influence of the surfactants including SDS, PEG6000, and CTAB on the morphology of the $\text{Al}(\text{OH})_3$ precipitates was shown in Figure 7. $\text{Al}(\text{OH})_3$ precipitates were prepared after aging treatment

of the sodium aluminate solutions containing $0.125 \text{ mol}\cdot\text{L}^{-1}$ $\text{Al}(\text{OH})_3$ nanoseed and $13.0 \text{ g}\cdot\text{L}^{-1}$ surfactant (SDS, PEG6000, or CTAB) for 10.0 h. Compared with those formed in the sole existence of $\text{Al}(\text{OH})_3$ nanoseed (Figure 6(f)), $\text{Al}(\text{OH})_3$ nanoparticles with smaller sizes were prepared in the presence of $\text{Al}(\text{OH})_3$ nanoseed and surfactants. $\text{Al}(\text{OH})_3$ nanoparticles with a diameter of 200–300 nm, 150–250 nm, and 80–100 nm were produced in the presence of SDS, PEG6000, and CTAB, respectively. The order of the influence of the surfactants on the formation of the $\text{Al}(\text{OH})_3$ nanoparticles was $\text{CTAB} > \text{PEG6000} > \text{SDS}$, and this phenomenon may be related to the interactions between the $\text{Al}(\text{OH})_3$ surfaces and the surfactants. The surfaces of $\text{Al}(\text{OH})_3$ formed in the concentrated NaOH solutions were negative charged owing to the adsorption of OH^- [13] which were easier to absorb the cationic surfactants as CTAB and difficult to absorb the nonionic surfactants as PEG6000 or the anionic surfactants as SDS.

Figure 8 shows the schematic diagram for the influence of $\text{Al}(\text{OH})_3$ nanoseed and the surfactants on the precipitation of $\text{Al}(\text{OH})_3$ from the sodium aluminate solution. Generally, the existence of $\text{Al}(\text{OH})_3$ nanoseed promoted the heterogeneous precipitation of $\text{Al}(\text{OH})_3$, and the adsorption of the surfactants as SDS, PEG6000 and CTAB, especially the cationic surfactant CTAB, on the surfaces of $\text{Al}(\text{OH})_3$ inhibited the growth of the $\text{Al}(\text{OH})_3$. The coinfluence of the $\text{Al}(\text{OH})_3$ nanoseed and CTAB on the precipitation of $\text{Al}(\text{OH})_3$ from the sodium aluminate solution led to the formation of the dispersive $\text{Al}(\text{OH})_3$ nanoparticles with a diameter of 80–100 nm.

4. Conclusion

$\text{Al}(\text{OH})_3$ nanostructures were synthesized from $\text{Al}(\text{OH})_3$ microagglomerates by dissolution of the $\text{Al}(\text{OH})_3$ microagglomerates in $9.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH at 115°C for 0.5 h followed by dilution and aging of the solution at room temperature. The experimental results indicated that the $\text{Al}(\text{OH})_3$

FIGURE 7: Morphology of $\text{Al}(\text{OH})_3$ nanoparticles formed in the presence of SDS (a), PEG6000 (b), and CTAB (c).

FIGURE 8: Sketch of the influence of $\text{Al}(\text{OH})_3$ nanoseed and surfactants on formation of $\text{Al}(\text{OH})_3$ nanostructures.

microspheres composed of nanoparticles were prepared in the blank experiment, while dispersive $\text{Al}(\text{OH})_3$ nanoparticles with a diameter of 80–100 nm were formed in the presence of $0.125 \text{ mol} \cdot \text{L}^{-1}$ $\text{Al}(\text{OH})_3$ nanoseed and $13.0 \text{ g} \cdot \text{L}^{-1}$ CTAB.

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