Effect of Anions during a Solid-state Reaction Preparation of Ammonium Aluminum Carbonate Hydroxide

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***Abstract*—Ammonium aluminum carbonate hydroxide (AACH) can be obtained from different anions of aluminum sources by a solid-state reaction. Anions play a crucial role on the properties of AACH. It is observed that best-crystallized AACH can be obtained from $Al_2(SO_4)_3$. Depending on the nature of anion present during synthesis, AACH obtained either from $Al_2(SO_4)_3$ or $AlCl_3$ has the similar phase transformations calcined at different temperatures, which is different from AACH obtained from $Al(NO_3)_3$. The specific surface area (S_{BET}) of alumina prepared by $Al_2(SO_4)_3$, which is obtained from the calcination of AACH at 500°C, is still in 610.6m2/g.**

Keywords-solid-state reaction; ammonium aluminum carbonate hydroxide; aluminum source

I. INTRODUCTION

Alumina is the most commonly used as adsorbents, catalysts, and catalyst supports [1.2], due to its good thermal stability, high specific surface area and modulated acid-base properties according to its synthesis conditions [3.4]. Usually, alumina is obtained by dehydroxylation of boehmite through precipitation from aluminum chloride or nitrate [5], hydrolysis of aluminum alkoxides [6.7], or thermal decomposition of AACH reported on our preious articles [8.9]. So far, the role of the anionic part of the aluminum salt on capability to form insoluble precursor powders for the preparation of alumina has been studied [10]. But a comparison of the influence of the anionic part of the aluminum source on capability of AACH precursor, including the crystallinity, morphology and thermal decomposition behavior, prepared by a solid-state reaction has not been reported.

The aim of this work is to study the effect of anions on AACH precursors obtained from a solid-state reaction. Meanwhile, the effect of anions on textural properties and morphology of alumina obtained by calcining AACH is also investigated.

II. EXPERIMENTAL

A. Preparation of Samples

All chemicals are analytical-grade regents without further purification. In a typical experiment, an amount of PEG-400 was added very slowly to NH_4HCO_3. The agate mortar was used for grinding the mixture of PEG-400 and NH_4HCO_3.

After the mixture was ground sufficiently, the powder of aluminum salt (using the same Al^{3+} molar ratio) was added. The final mixture was ground at room temperature for 20 min, transferred to a Teflon-lined stainless-steel autoclave and placed in an oven at 80°C. After 7h, the solid was filtered off, washed with deionized water and anhydrous ethanol to move the impurities, and dried at 120°C in a vacuum oven for 2h. The PEG-400 was removed by calcination in air at 500°C for 4h with heating rate of 2°C/min. The effect of aluminum salts was examined as detailed in Table 1.

TABLE I. THE EFFECT OF ANIONS ON PREPARING DIFFERENT ALUMINA NANOSTRUCTURE SAMPLES

Sample	Materials		
	Aluminum salts (g)	***NH_4HCO_3 (g)***	***PEG-400 (mL)***
Al-S	$Al_2(SO_4)_3\cdot 18H_2O$, 16.66	15.80	0.16

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Sample	Materials		
	Aluminum salts (g)	***NH_4HCO_3 (g)***	***PEG-400 (mL)***
Al-N	$Al(NO_3)_3 \cdot 9H_2O$, 18.76	15.80	0.16
Al-Cl	$AlCl_3 \cdot 6H_2O$, 12.07	15.80	0.16

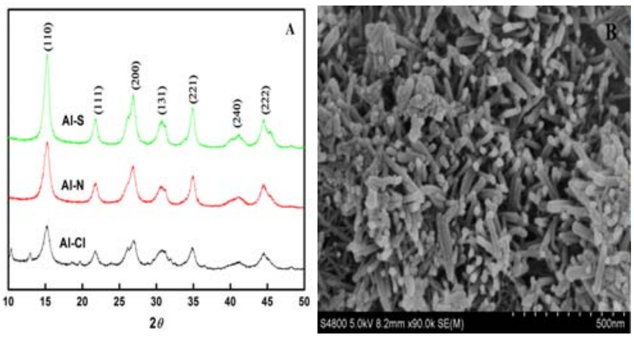
B. Characterization

X-ray powder diffraction (XRD) analysis was carried out with a PANalytical X'Pert PRO MPD diffractometer using a Cu Kα radiation (λ=1.54060Å) operating at 40kV and 40mA. A scanning electron microscope (SEM) (Hitachi S-4800) coupled with an electron dispersive X-ray (EDX) was used to perform elemental analysis. The N_2 adsorption and desorption isotherms were measured on a Micromeritics Tristar 3000 instrument. Specific surface area determination was made using the BET isotherm. Fresh samples were vacuum dried before the adsorption measurement.

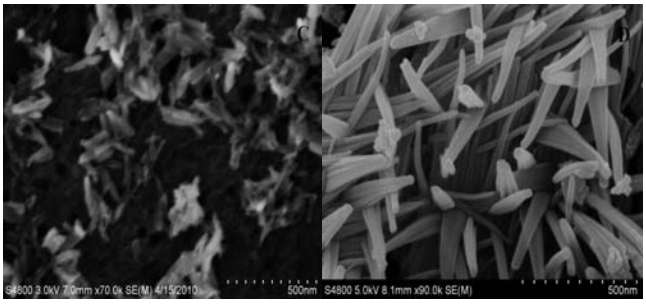
III. RESULTS AND DISCUSSION

A. Effect of anions on phase identification and morphology of as-synthesized precursors

The XRD patterns of the precursors are shown in Fig. 1(A), and the XRD patterns of all as-synthesized samples can be indexed to crystalline ammonium aluminum carbonate hydroxide (AACH) with a composition of $NH_4Al(OOH)HCO_3$ (JCPDS card no. 00-042-0250). As shown in Fig. 1(A), using the $Al_2(SO_4)_3$ as aluminum source results in best-crystallized AACH compared to $Al(NO_3)_3$ and $AlCl_3$.The effect of aluminum sources on the morphology of the precursors is also investigated (shown in Figs. 1(B), 1(C) and 1(D)). It is seen that the precursor obtained from $Al_2(SO_4)_3$ exhibites a particle morphology with some irregular rodlike particles. The length of the fiber is about 120nm, and the diameter is about 25nm. It means that crystals grew quicker along the longitudinal direction than the diametric direction. The precursor obtained from $Al(NO_3)_3$ also displays a particle morphology with some smaller rodlike. However, the precursor obtained from $AlCl_3$ exhibites a multilayered nanofiber morphology. The nanofibers are not tangled, and the nanofibers have a smooth surface. The top of the nanofiber is smaller than the bottom of the nanofiber. The length of the fiber is about 370nm. The above results indicate anions play an important role in controlling the crystallinity and morphology of AACH.



(A) (B)



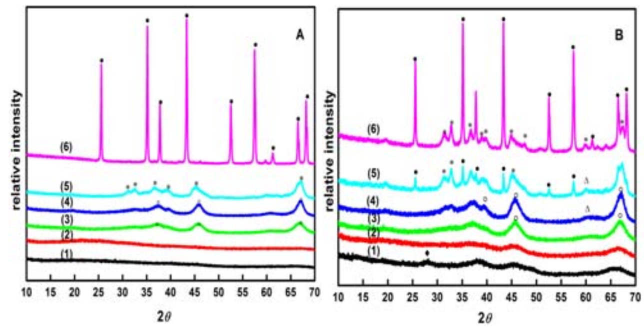
(C) (D)

Figure 1. The SEM photographs of the samples (B) Al-S, (C) Al-N and (D) Al-Cl.

B. Effect of anions on thermal decomposition behaviors of as-synthesized precursors

The decomposition of AACH phase can be described by the following reaction:

$$2NH_4AlO(OH)HCO_3 \rightarrow Al_2O_3 \cdot nH_2O + 2CO_2 + 2NH_3 + (3-n)H_2O$$



(A) (B)

Figure 2. (A)X-ray diffraction patterns of AACH obtained from $Al_2(SO_4)_3$ after heat treatment at different temperatures: (1) 300°C; (2) 400°C; (3) 800°C; (4) 900°C; (5) 1000°C; (6) 1100°C. (B) X-ray diffraction patterns of AACH obtained from $Al(NO_3)_3$ after heat treatment at different temperatures: (1) 300°C; (2) 700°C; (3) 800°C; (4) 900°C; (5) 1000°C; (6) 1100°C. ((＊) θ-Al_2O_3; (·) α-Al_2O_3; (◆) pseudo-boehmite; (。) γ-Al_2O_3; (Δ) δ-Al_2O_3)

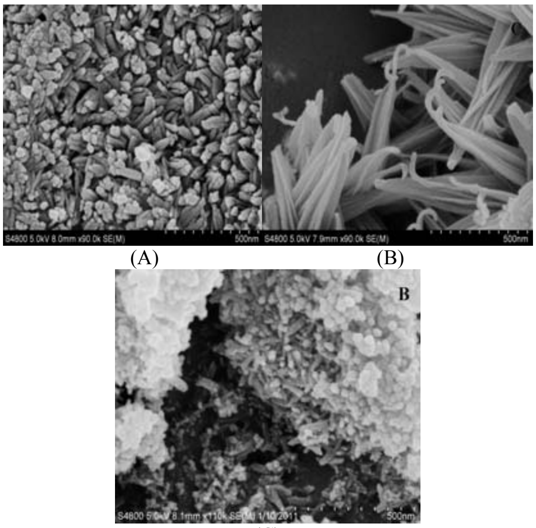
Fig. 2(A) shows the X-ray diffraction patterns obtained from the calcination of AACH obtained from $Al_2(SO_4)_3$ in the temperature range 300-1100°C. During the process of calcination, the following series of phase transformations take place to form α-Al_2O_3[11,12]: $NH_4AlO(OH)HCO_3 \rightarrow$ amorphous $Al_2O_3 \rightarrow \gamma$-$Al_2O_3 \rightarrow \theta$-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$. At 300-700°C, amorphous Al_2O_3 appears. At 800°C, the γ-Al_2O_3 starts to emerge, and it becomes more apparent at 800-900°C. At 1000°C, the θ-Al_2O_3 starts to emerge. With a higher calcination temperature at 1100°C, the α-Al_2O_3 appears. AACH obtained from $Al_2(SO_4)_3$ and $AlCl_3$ have the similar phase transformations. However, phase transformations of AACH obtained from $Al(NO_3)_3$ are different. Fig. 2(B) shows the X-ray diffraction patterns obtained from calcination of AACH obtained from $Al(NO_3)_3$ in the temperature range 300-1100°C. During thermal treatment, the following series of phase transformations take place to form α-Al_2O_3 [11,12]: $NH_4AlO(OH)HCO_3 \rightarrow Al_2O_3 \cdot nH_2O \rightarrow \gamma$-$Al_2O_3 \rightarrow \delta$-$Al_2O_3 \rightarrow \theta$-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$. At 300°C, both pseudo-boehmite and γ-

Al_2O_3 patterns appear. At 400°C, the γ-Al_2O_3 starts to emerge, and it becomes more apparent at 500-800°C.At 1000°C, γ-Al_2O_3 disappears, and δ-Al_2O_3, θ-Al_2O_3, α-Al_2O_3 start to emerge. With a higher calcination temperature at 1100°C, the θ-Al_2O_3 and α-Al_2O_3 appear. It can be proved that the phase transformations of AACH are closely related with anions of aluminum sources.

C. Effect of anions on textural properties and morphology of alumina

TABLE II. TEXTURAL PROPERTIES OF SOME REPRESENTATIVE SAMPLES CALCINED AT 500°C FOR 4H.

Sample	**Textural Properties**		
	BET specific surface area($m^2 \cdot g^{-1}$)	***Pore volume($mL \cdot g^{-1}$)***	***Average Pore Size(nm)***
Al-S	610.6	1.1	7.56
Al-N	303.6	1.0	10.62
Al-Cl	420.2	1.2	8.18



(A) (B) (C)

Figure 3. The SEM photographs of the samples (A), (B) and (C) obtained from $Al_2(SO_4)_3$, $Al(NO_3)_3$ and $AlCl_3$ calcined at 500°C for 4h

Table 2 lists textural properties measured for samples obtained from $Al_2(SO_4)_3$, $Al(NO_3)_3$ and $AlCl_3$ calcined at 500°C for 4h. The pore volume should be attributed to the intercrystallite voids of the randomly stacked alumina nanostructure. The surface area of the sample obtained from $Al_2(SO_4)_3$ has the maximum value. Accordingly, the average pore size of the sample obtained from $Al_2(SO_4)_3$ has the minimum value of 7.56nm. The effect of anions on the morphology of alumina is also investigated. The Fig. 3 shows the SEM photographs of the sample obtained from $Al_2(SO_4)_3$, $Al(NO_3)_3$ and $AlCl_3$ calcined at 500°C for 4h. It is seen that the sample obtained from $Al_2(SO_4)_3$ exhibits a particle morphology with the aggregation of nanorod particles. The length of the aggregation of some nanorod particles is about 120nm, and the diameter is about 40nm. The sample obtained from $Al(NO_3)_3$ shows that some rodlike particles keep partially as before, and another particles break into fragments during the calcination process compared to the precursor (see Fig. 1(C)). And the sample obtained from $AlCl_3$ presents curving nanowires on the top of the nanofibers during the calcination process, which reveals that the nanofiber is consisted with multilayer structure which may be formed by assembling of nanowires [13].The equations are an exception to the prescribed specifications of this template. You will need to determine whether or not your equation should be typed using either the Times New Roman or the Symbol font (please no other font). To create multileveled equations, it may be necessary to treat the equation as a graphic and insert it into the text after your paper is styled.

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