Hydrothermal Synthesis of Ammonium Aluminum Carbonate Hydroxide (AACH) Nanoplatelets and Nanofibers pH-Controlled Morphologies

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Abstract—$NH_4Al(OH)_2CO_3$ **precursors were prepared using** $Al(NO_3)_3$ **and** NH_4HCO_3 **as raw materials. The structural, morphological, and porous properties of the materials were investigated by BET, X-ray Diffraction (XRD), and Scanning Electron Microscope (SEM).The morphology and aspect ratios of resulting AACH nanoparticles were significantly influenced by the pH values in the preparation of solid precipitates.There were two kinds of morphology present, nanofibers and nanoplates. After thermal treatment at 550 $^{\circ}$C in air for 4 hours, the morphologies of the nanostructures werewell preserved while the crystal structure was converted to γ-alumina.**

Keywords-Ammonium Aluminum Carbonate Hydroxide; pH values; morphology

I. INTRODUCTION

Alumina has received special attention due to their thermal and chemical stability, high specific surface area, surface acidity, low cost and their potential in many applications[1] such as electronics, metallurgy, optoelectronics ,fine ceramic composites and catalyst supports[2,3,4,5]. The properties of Al_2O_3 are determined predominantly by crystal structure, composition, particle size and morphology. Therefore, the synthesis of Al_2O_3 with well controlled composition, size and morphology is of great significance for their applications[6].

Presently, a lot of work studied the preparation of the morphology-controlled alumina via a AACH precursor due to its special crystal structure[7,8,9,10], which are benefits to the preparation of the morphology-controlled and mesopores-remained Al_2O_3 products. In the present work, we study the effect of pH values on Ammonium aluminum carbonate hydroxide synthesised by hydrothermal homogeneous precipitation method. The pH value plays a key role on the morphology and textural porperties of AACH precursor and alumina.

II. EXPERIMENTAL

A. Material Synthesis

The synthesis of alumina precursors and samples was conducted using a hydrothermal homogeneous precipitation method. All regents are analytical-grade. In a typical synthetic procedure, a certain amount of $Al(NO_3)_3 \cdot 9H_2O$ was added to 100 mL deionized water under vigorous stirring, then 2.0 mol/mL NH_4HCO_3 solution was added slowly. At last, ammonia solution was added into the mixture until pH value of the mixture was 7.0~11.0. Then it was kept in an Electric Water Bath at 65 $^{\circ}$C to allow crystallization for 24 h. The product was collected by centrifugation, washed with distilled water and absolute ethanol several times to remove the impurities, and finally dried at 80 $^{\circ}$C in an oven for 24 h. The samples were denoted as (see Table 1).

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

Sample	Materials		
	Aluminum salts (mol/mL)	NH_4HCO_3 (mol/mL)	pH values
a	$Al(NO_3)_3 \cdot 9H_2O$ 0.2	2.0	7.0
b	$Al(NO_3)_3 \cdot 9H_2O$ 0.2	2.0	9.0
c	$Al(NO_3)_3 \cdot 9H_2O$ 0.2	2.0	11.0

TABLE II. TEXTURAL PROPERTIES OF SOME REPRESENTATIVE SAMPLES CALCINED AT 550°C

Samples	Textural Properties		
	BET specific surface area($m^2 \cdot g^{-1}$)	Pore volume(mL·g^{-1})	Average Pore Size(nm)
a	257.03	0.86	12.67
b	232.82	0.51	8.69
c	310.43	1.05	10.77

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 40 kV and 40 mA. 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 the pH values on the morphology of AACH products

The crystalline phase of the as-prepared samples was identified by powder X-ray diffraction. Curve (a), (b) and (c) in Fig. 1 shows the typical XRD patterns of the as-synthesized samples prepared at 80 °C for 24 h at pH ≈7.0, 9.0, and 11.0 respectively. All the diffraction peaks can be identified as the crystalline AACH (JCPDS card 042-0250). The chemical reaction occurs as follow[11]:

$$Al^{3+}+4NH_4HCO_3=NH_4AlO(OH)HCO_3\downarrow+3CO_2\uparrow+H_2O+3NH_4^+$$

The pH value of the initial solution has great effect on the size and morphology of the hydrothermal products. The SEM images of precursors a, b and c, which are synthesized in different pH values are shown in Fig.1(B),(C),(D). The three precursor samples have different morphology. Which can be easily distinguished by SEM spectra. Samples (a) and (b)

possess rod-like architecture with a diameter form 40 nm to 100 nm,and the length form 300 nm to 700 nm. The precursor particles become smaller as the pH values increased.
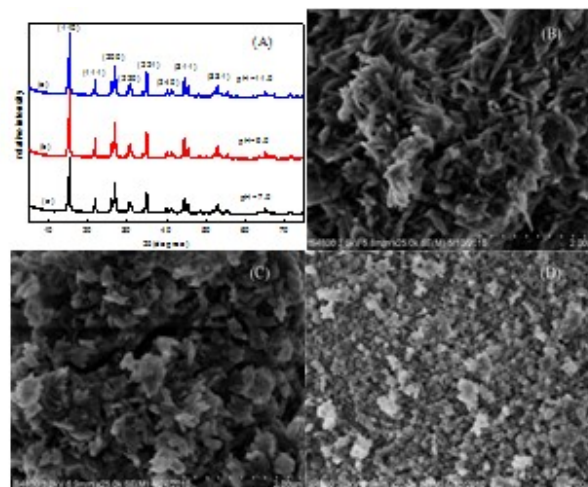

Figure 1. (A)X-ray diffraction patterns of AACH synthesized in different pH values and the SEM photographs of the samples (B) pH=7.0, (C) pH=9.0, (D) pH=11.0.

B. Effect of the pH values on textural properties and morphology of alumina

To investigate the specific surface area and porous nature of the γ-Al_2O_3 samples obtained by calcining at 550 °C for 4 h, Brunauer-Emmett-Teller (BET) gas-sorption measurements were carried out. The structural parameters derived from these isotherms are summarized in Table 2. Specific surface area of sample (c) is higher (310.43 $m^2.g^{-1}$) than sample (a)(257.03 $m^2.g^{-1}$) and (b) (232.82 $m^2.g^{-1}$) according to the decrease of particle size, and the sample (b) shows a minimum average pore size when pH=9.0. Figure 2 shows the nitrogen adsorption-desorption isotherms of γ-Al_2O_3 samples (a),(b)and (c). It can be seen that all of these samples reveal a type-IV isotherm with an H1 hysteresis loop, indicating that they belong to mesoporous material. The well-developed H1 hysteresis loop in the case of sample(a),(b) and (c) is believed to be related to the capillary condensation in large pore channels with possible channel modulation[12]. The results of their BJH pore size distribution (Figure 2(A)) show the materials have uniform porous size distribution centered at ca.4.2 nm, which is consistent with their results of SEM. The capillary condensation steps for the samples ranging from (a) to (c) are shifted to different relative pressures, indicating an difference in the size of mesopores. As can be seen from these figures, the textural properties of γ-Al_2O_3 are highly dependent on the alumina precursors synthesised pH values.
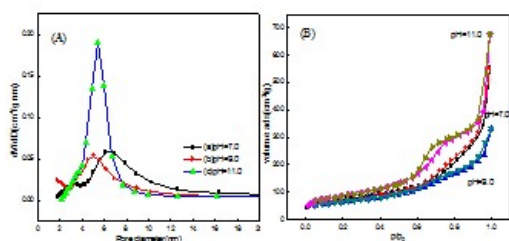
Figure 2. N₂ adsorption-desorption isotherm, and pore size distribution for γ-Al₂O₃ prepared at different pH values

Figure 3 presents the SEM images of samples (a), (b), (c) alumina synthesized in different pH values. It can be seen that the sample (a) in Fig.3(A) are made of uniform microfibers with the length of about 300-500nm and the width of less than 100nm.There are also some little patchs around the rod-like nanofibers ,which were formed during the calcination process. Sample (b) present the same morphology as sample(a),but its overall dimensions was smaller. It is seen that the sample(c) exhibits a particle morphology with the aggregation of nanorod particles.
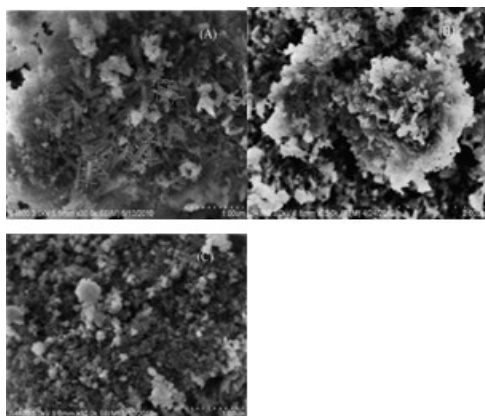

Figure 3. The SEM photographs of alumina synthesized in different pH values(A)pH=7.0,(B) pH=90, (C) pH=11.0.

IV. CONCLUSION

Ammonium aluminum carbonate hydroxide and γ-Al₂O₃ had been successfully synthesized by hydrothermal process of Al(NO₃)₃·9H₂O with the NH₄HCO₃. The study showed that the morphology and aspect ratios of resulting AACH nanoparticles were significantly influenced by the pH values. Nanofibers were synthesised at the pH=7.0 and 9.0. While, nanoplates were synthesised at the pH value of 11.0. However, the detailed mechanism is not clear and still under way nowadays.

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