



# Meso/macroporous $\gamma$ -Al<sub>2</sub>O<sub>3</sub> fabricated by thermal decomposition of nanorods ammonium aluminium carbonate hydroxide

Guang-Ci Li, Yun-Qi Liu<sup>\*</sup>, Li-Li Guan, Xiao-Fu Hu, Chen-Guang Liu

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, CNPC, China University of Petroleum, Qingdao 266555, PR China

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## ABSTRACT

Through exploring the reaction parameters during the synthesis of the AACH, rod-like ammonium aluminium carbonate hydroxide (AACH) with high crystallinity has been successfully prepared via a facile hydrothermal method. The synthesis parameters like time, the molar ratio of NH<sub>4</sub>HCO<sub>3</sub>/Al and the properties of starting materials were systematically investigated. The structure was characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), IR and transmission electron microscopy (TEM). The experimental results display that the obtained  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> materials possess meso/macroporosity and large pore volume, which are mainly attributed to the removal of gas molecules during the decomposition of AACH. Moreover, using the rod-like AACH as precursor,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanorods were obtained via a low-temperature thermal decomposition method.

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## 1. Introduction

Transition aluminas have received special attention due to their thermal and chemical stability, high specific surface area, surface acidity, low cost and their potential in many applications such as catalyst supports, adsorbents, ceramics and abrasives [1–3]. When Transition aluminas like  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are used as catalyst support, it is very important to introduce meso/macroporosity and high pore volume because these pore properties play a key role for the performance of catalyst, in particular in reactions involving large molecules. For example, in refinery industry, it is notorious that catalysts used for residual oil hydrotreating processes deactivate predominantly due to pore blocking resulted from high contents of metal poisoners, heteroatoms, and asphaltenes in heavy fractions [4]. To avoid pore blocking problem, one strategy is to introduce meso/macro pores and high pore volume into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports. Several methods have been proposed for the synthesis of high quality traditional aluminas to avoid rapid catalyst deactivation [5,6]. However, traditional aluminas possess relatively low surface area (less than 250 m<sup>2</sup> g<sup>-1</sup>) and broad pore size distribution, which limit their catalytic applications [7], and besides, the increase in pore size leads to lower surface area. Thus, nowadays researches in this field focused more on the synthesis of mesoporous alumina using

various templates, such as surfactants [8–11], carboxylic acids [12], and single organic molecules [13–16].

Ammonium aluminium carbonate hydroxide (AACH, with formula NH<sub>4</sub>Al(OH)<sub>2</sub>CO<sub>3</sub>) has a structure similar to the mineral dawsonite (NaAl(OH)<sub>2</sub>CO<sub>3</sub>), which is composed of the AlO<sub>2</sub>(OH)<sub>4</sub> chains of octahedra [17–19]. As AACH can transform into aluminium oxide with different crystal structures simple through moderating thermal treatment temperatures, it could be a promising precursor for the preparation of aluminium oxide with special properties. Methods for preparation of AACH include gas–liquid, gas–solid, solid–solid, and liquid–liquid [20]. The most popular one is liquid–liquid precipitation method. In this method, AACH is typically prepared by precipitation of aqueous solutions of aluminium salts (NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, AlCl<sub>3</sub>) or Al(OH)<sub>3</sub> suspensions with aqueous solutions of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> or NH<sub>4</sub>HCO<sub>3</sub> [21–28]. However, due to the low crystallinity and small size of AACH particles reported in the literature, it was difficult to obtain the meso/macroporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> materials with large pore volume for processing heavy oil in petrochemical industry. Therefore, it is highly deserved to find a method to prepare high crystalline AACH with large crystal size.

Herein, we report first a novel method for preparation of rod-like AACH via hydrothermal treatment of a commercial aluminium hydroxide xerogel (AHx) in an aqueous solution of NH<sub>4</sub>HCO<sub>3</sub>. After that, the formation and phase transformation process from AACH to aluminium oxide was studied. Both AACH and rod-like aluminium oxide were characterized thoroughly with advanced characterization techniques like XRD, SEM, IR and TEM. Finally, the

<sup>\*</sup> Corresponding author. Tel.: +86 532 86981861; fax: +86 532 86981787.

E-mail address: [liuyq@upc.edu.cn](mailto:liuyq@upc.edu.cn) (Y.-Q. Liu).

formation mechanism for bimodal porosity of  $\gamma$ - $\text{Al}_2\text{O}_3$  was proposed.

## 2. Experimental

### 2.1. Preparation of AACH and $\gamma$ - $\text{Al}_2\text{O}_3$

#### 2.1.1. Preparation of rod-like AACH

In a typical synthesis, 0.30 g of AHx powder ( $\text{Al}_2\text{O}_3$  70 wt%, Henghui Chemical Engineering Co., Ltd., Shandong, China) was dissolved into an 15 ml aqueous solution of  $\text{NH}_4\text{HCO}_3$ , the mol ratio  $\text{NH}_4\text{HCO}_3/\text{Al}$  have been easily adjusted from 0.7 to 7. The pH value of solution was controlled to ca. 10.5 using aqueous  $\text{NH}_3\cdot\text{H}_2\text{O}$ . Then the final mixture was transferred into 40 ml Teflon-lined stainless autoclave and kept at a temperature ranges from 75 °C to 150 °C for 12 to 48 h. Finally, the products were collected and washed several time with  $\text{H}_2\text{O}$ . The resulting solid was dried under vacuum at 60 °C for 8 h.

#### 2.1.2. Preparation of rod-like $\gamma$ - $\text{Al}_2\text{O}_3$

$\gamma$ - $\text{Al}_2\text{O}_3$  were prepared by first mixing the obtained AACH powders with aqueous acetic acid solution (20.0 wt%) to a suitable viscosity and then extruded in a radial extruder with a 1.6 mm sieve. After extrudation, the extrudates were dried in air at 80 °C overnight. Then the dried samples were calcined in air at different temperatures ( $T = 350, 500, 600, 700, 800, 900$  °C) for 2 h at 2 °C  $\text{min}^{-1}$  heating ramp. The calcined samples were labeled as A-350, A-500, A-600, A-700, A-800, A-900, according to the temperatures of calcination. For comparison, two commercial aluminas, which came from Henghui Chemical Engineering Co., Ltd., (China) and Condea Chemical Co., (Germany), were selected. Both of them were obtained by heating their precursors at 600 °C for 2 h, and the calcined samples were labeled as A-600-1 and A-600-2, respectively.

### 2.2. Characterization

The crystal structure was identified with the X-ray powder diffraction (XRD; Panalytical X'Pert Pro MPD, Cu  $K\alpha$  radiation,  $\lambda = 1.5406$  Å). The morphology and structure of sample powder were observed by scanning electron microscopy (SEM; Hitachi S-4800) and transmission electron microscopy (TEM; JEOL JEM-2100UHR), respectively. The spectral shapes of the samples were identified by Fourier transform infrared spectroscopy (FTIR; Newus Nicolet, USA) at room temperature using KBr disks. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in a NETZSCH STA 449C analyzer, ramping the temperature from 30 to 600 °C with a heating rate of 20 K  $\text{min}^{-1}$ . The pore property of samples was measured through nitrogen adsorption/desorption isotherms (Micromeritics Tristar 3020 nitrogen adsorption apparatus) and mercury intrusion method (Micromeritics AUTOPORE 9500 porosimeter), respectively. Prior to measurement, all the samples were degassed under vacuum at 120 °C over 8 h.

## 3. Results and discussion

### 3.1. Effects of reaction conditions on the formation of AACH

#### 3.1.1. Hydrothermal temperature

Fig. 1 shows the XRD patterns of the samples prepared at various hydrothermal temperatures. It can be found that the main composition for all the samples is  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$  (JCPDS 01-076-1923). However, the sample prepared at 105 °C is composed of  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$  phase. As seen from Fig. 1, low temperature (75 and 90 °C) is not favorable for forming AACH. This may be due

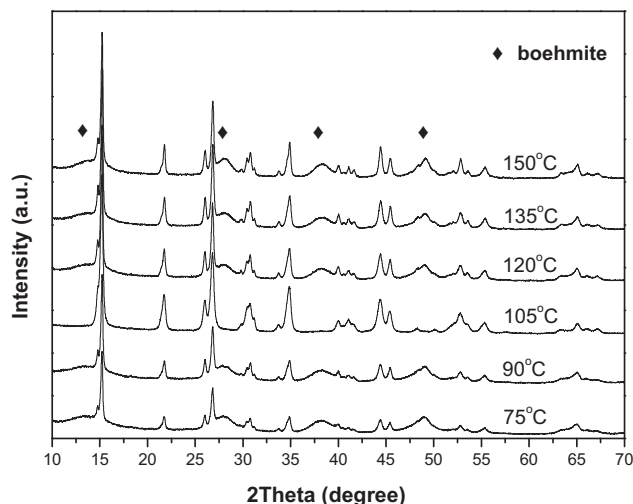


Fig. 1. The XRD patterns of samples prepared at different hydrothermal temperatures ( $\text{NH}_4\text{HCO}_3/\text{Al}$ : 7.0, reaction time: 24 h).

to that at low temperature AHx particles cannot deliberate to form active  $\text{Al}(\text{OH})_4^-$  ions completely. Thus, some unreacted boehmite phase (JCPDS 00-049-0133) can be found in the samples. Although relatively high temperature may improve reaction, a portion of  $\text{NH}_3$  and  $\text{CO}_2$  molecules would escape from solution at a higher temperature due to the decomposition of  $\text{NH}_4\text{HCO}_3$ , inducing an decrease in pH value of system. Low pH value can also affect the formation of  $\text{Al}(\text{OH})_4^-$  ions. Therefore, the optimal temperature for the preparation of AACH was selected as at 105 °C.

#### 3.1.2. Molar ratio of $\text{NH}_4\text{HCO}_3/\text{Al}$

Fig. 2 shows the XRD patterns of the products obtained at different  $\text{NH}_4\text{HCO}_3/\text{Al}$  ratios. It can be found that the diffraction peaks of boehmite became lower with increasing the amount of  $\text{NH}_4\text{HCO}_3$ . When  $\text{NH}_4\text{HCO}_3/\text{Al}$  ratio reached 7.0, the diffraction peaks of boehmite disappeared and all the peaks can be identified to  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$ , and no diffraction peaks for impurity were observed. The sharp peaks indicate that the AACH has a high crystallinity.

The AACH particles obtained at 105 °C for 48 h exhibited rod-like morphologies with large aspect ratio (Fig. 3a and b). The

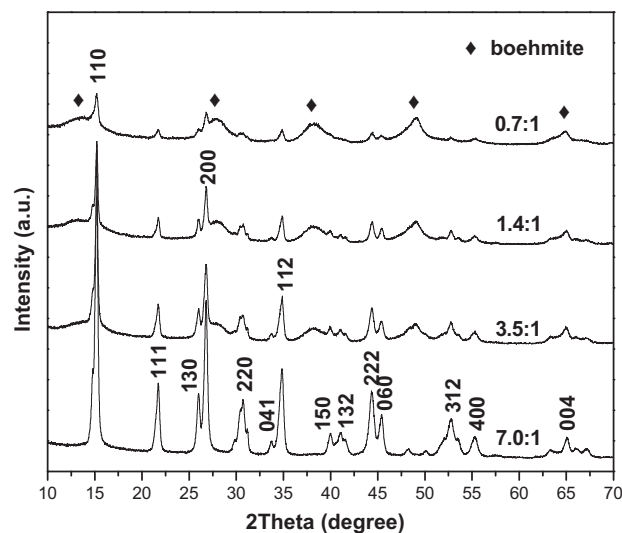


Fig. 2. The XRD patterns of samples prepared at various molar ratio of  $\text{NH}_4\text{HCO}_3/\text{Al}$  (reaction temperature: 105 °C, reaction time: 24 h).

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