Vacuum 133 (2016) 1–6

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Synthesis and characterization of mesoporous alumina with high specific area via coprecipitation method

Lili Zhang [a], Yusheng Wu [a, *], Linnan Zhang [b], Yuzheng Wang [a], Mingchun Li [a]

[a] *College of Materials Science and Engineering, Shenyang University of Technology, Shenyang 110870, China*
[b] *College of Science, Shenyang University of Technology, Shenyang 110870, China*

ARTICLE INFO

Article history:
Received 7 July 2016
Received in revised form
9 August 2016
Accepted 10 August 2016
Available online 12 August 2016

Keywords:
Mesoporous
γ-Al_2O_3
Coprecipitation
AACH

ABSTRACT

Mesoporous γ-Al_2O_3 with high specific surface area is prepared via calcination of $NH_4Al(OH)_2CO_3$ (AACH). The AACH is obtained by coprecipitation route with NH_4HCO_3 and $NH_4Al(SO_4)_2$ as raw materials. The effects of pH value and calcination temperature on the characterization of products are investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N_2 adsorption-desorption method and Transmission electron microscopy (TEM). The results show that mesoporous γ-Al_2O_3 obtained by calcining AACH at 500 °C for 4 h exhibits high specific surface area of 571.32 m^2/g, a pore volume of 0.75 cm^3/g and pore size of 6.15 nm. With the calcining temperature increase, the specific surface area and pore volume decrease, and the pore size increase. When the calcining temperature elevates up to 900 °C which is higher than the application temperature of most active agents, the specific surface area of 150.67 m^2/g, the pore volume of 0.51 cm^3/g and pore size of 9.65 nm was obtained.

1. Introduction

Mesoporous γ-Al_2O_3 is widely applied to adsorbents, chemical and biological separation, catalyst and catalyst support owing to its excellent properties such as porosity, high specific area and chemical activity [1–4]. At present, there are many materials as aluminum sources to synthesis γ-Al_2O_3, for example $Al(NO_3)_3$, $Al_2(SO_4)_3$, $NH_4Al(SO_4)_2$, $AlCl_3$, $NaAlO_2$ and so on. Kim [5] used $Al(NO_3)_3 \cdot 9H_2O$ as aluminum source by sol-gel method to prepare mesoporous γ-Al_2O_3 with the specific area of 322 m^2/g. Zhong et al. [6] used $AlCl_3$ and $NaAlO_2$ as aluminum sources to prepare mesoporous alumina with the specific area of 309 m^2/g and pore volume of 0.31 cm^3/g. In our previous experiments [7], $NaAlO_2$ as aluminum source, mesoporous γ-Al_2O_3 prepared by a reverse precipitation method was of specific surface area of 340 m^2/g and pore volume of 0.9 cm^3/g at the calcining temperature of 500 °C for 4 h.

The mesoporous γ-Al_2O_3 synthesized with the above aluminum sources has excellent properties. However, these aluminum sources are expensive so that it is difficult to realize the industrialization with these ways. Recently, coal fly ash as a cheap aluminum source to synthesis γ-Al_2O_3 has attracted extensive attention [8–10]. Coal fly ash is the major coal solid waste and its utilization rate is very low so that it is generally dumped in lands and poses a serious threat to the environment [11,12]. Therefore, the synthesis of alumina from coal fly ash is environmentally and scientifically significant for disposing and utilizing waste materials [11,12]. Coal fly ash contains various impurities such as Fe_2O_3, Na_2O, K_2O, P_2O_5, MaO, CaO, MgO and TiO_2 [13], so it is difficult to synthesis pure alumina by a simple acid or alkali treatment. In our previous experiments [14,15], one method of obtaining alumina with coarse particle from coal fly ash is to synthesize aluminum ammonium sulfate (alum) as an intermediate product through sintering coal fly ash with ammonium sulfate. The advantage of the alum as an intermediary is to improve its purity through a straightforward recrystallization process. The synthesis of alumina with alum as the aluminum sources has been reported in the literature [16–18]. Furthermore, AACH is one of alumina precursors, which is widely used to synthesize α-alumina nanostructure [19–21]. However, "the synthesis of γ-Al_2O_3 with high specific area by thermal decomposition of AACH" is often ignored.

Based on the analysis above, the purpose underlying the present work is to explore crystallizing rule of AACH from alum solution and to synthesize alumina with high specific surface area. Hence the effects of pH value and calcining temperature on the characterization of products have been investigated.

---

* Corresponding author.
E-mail address: henanwys@sina.com (Y. Wu).

http://dx.doi.org/10.1016/j.vacuum.2016.08.005

2. Experimental

2.1. Experimental materials

Ammonium aluminum sulfate (alum) as raw materials was obtained through sintering coal fly ash with ammonium sulfate, and the relevant processes can be found in the literature [14]. To improve the purity of alum, the alum was put into sulfuric acid solution until the alum completely dissolved. Then cooling cycle to room temperature, re-precipitate formed. The recrystallization process then repeated three times, relatively pure alum is obtained. The XRD pattern of alum (JCPDS, No. 23-0001) obtained through above processes is shown in Fig. 1. No impurity phases are found. The mass percent of alumina from the alum obtained is confirmed to be greater than 21.3% by ICP analysis (shimadzu ICPE-8100).

Ammonium hydrogen carbonate (NH_4HCO_3) and other chemicals used in this study were of analytical grade and purchased from national Pharmaceutical Group, China.

2.2. Experimental process and analytical method

$NH_4Al(SO_4)_2$ obtained by the above method and NH_4HCO_3 were dissolved into distilled water to obtain the staring solutions and the concentrations of NH_4HCO_3 and $NH_4Al(SO_4)_2$ were 2 mol/L and 0.2 mol/L, respectively. In coprecipitation experiments, 250 ml $NH_4Al(SO_4)_2$ solution was pumped into 100 ml NH_4HCO_3 solution at a rate of 10 ml/min under magnetic stirring at 60 °C. During the experiment, pH value of the reaction system was remained in predetermined value by adding ammonium hydroxide. The resultant precursors were collected by vacuum filtration, followed by washing four times with hot distilled water, dried at 110 °C for 2 h. And then the dried powder was calcinated at various temperatures (500 °C, 700 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C) at a heating rate of 2 °C/min, respectively, and held at these temperatures for 4 h in air.

Structural phase analysis of the sample was performed by an XRD-7000 equipped with Cu Kα radiation. A continuous mode was used to collect 2θ data from 10° to 80° with a scanning rate of 8°/min. Fourier-transform infrared (FTIR) date was collected by a Bruker IF S66V spectrometer in a frequency range of 4000–400 cm^{-1} at the frequency step size of 4 cm^{-1}. Full adsorption-desorption isotherms of nitrogen at 77 K of the calcined samples were measured at various partial pressures by a V-Sorb 4800P Surface Area and Pore Porosimetry Analyzer. The nitrogen uptake in the partial pressure region below 0.30 provided a linear fit to the Brunauer-Emmett-Teller (BET) equation. Total pore volumes were determined at a partial pressure of 0.99. Pore size distributions were obtained by fitting the Barret-Joyner-Halenda (BJH) model of the desorption isotherms. Before the BET/BJH measurements, all the samples were degassed at 200 °C for 4 h. The morphology of the material was studied by transmission electron microscopy (TEM, JEOL-3010) operated at an accelerating voltage of 300 kV.

3. Results and discussions

3.1. Characterization of AACH

The XRD patterns of precursors obtained in various pH solutions are shown in Fig. 2. It can be seen that all peaks are consistent with crystalline AACH in chemical formula $NH_4Al(OH)_2CO_3$ (JCPDS, No. 76-1923). No impurity phases are found, which indicates the AACH synthesized in this experiment is high pure. At pH = 8, the crystalline of AACH is relatively low. With the pH value of the reaction solution increasing from 8.5 to 10, XRD patterns have little change and the peak intensity strengthen, which indicates that pH value has slight influence on product crystalline degree and the AACH with well-crystallized can be obtained at pH value from 8.5 to 10. The reaction in the experiment can be expressed as follow [22]:

$$NH_4Al(SO_4)_2 + 4NH_4HCO_3 \rightarrow NH_4Al(OH)_2CO_3\downarrow + 2(NH_4)_2SO_4 + 3CO_2\uparrow + H_2O \tag{1}$$

The FTIR patterns of the precursors obtained at different pH values are shown in Fig. 3. The peaks at 3444 cm^{-1} and 1726 cm^{-1} belong to stretching vibration and bending of physical absorption water. The absorption peaks in the region 3013–3172 cm^{-1} belong to symmetric bending vibrations of NH_4^+ and around 1393 cm^{-1} is ascribed to asymmetric bending modes. The absorption peaks at 1451 cm^{-1} and 1552 cm^{-1} are corresponded to asymmetric stretching vibrations of CO_3^{2-}, the existence of obvious split of the double degenerate peak is because that the CO_3^{2-} in the AACH belong to the structural carbonate group. The peak at 1106 cm^{-1} belongs to vibration of internal constitution water of AACH. The absorption peaks at 739 cm^{-1}, 635 cm^{-1} and 492 cm^{-1} are

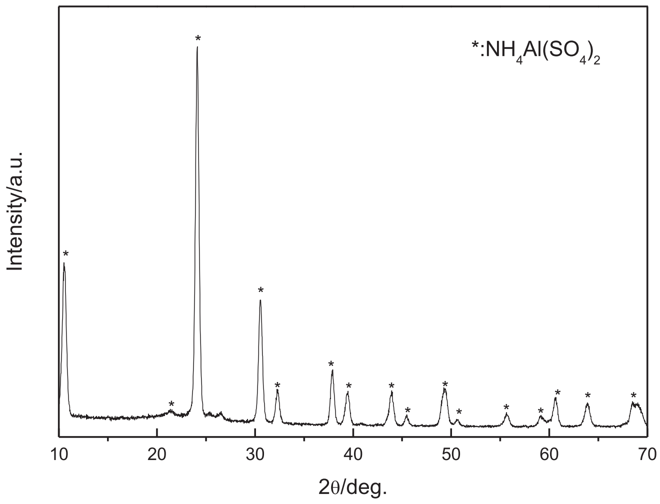

Fig. 1. XRD patterns of alum.

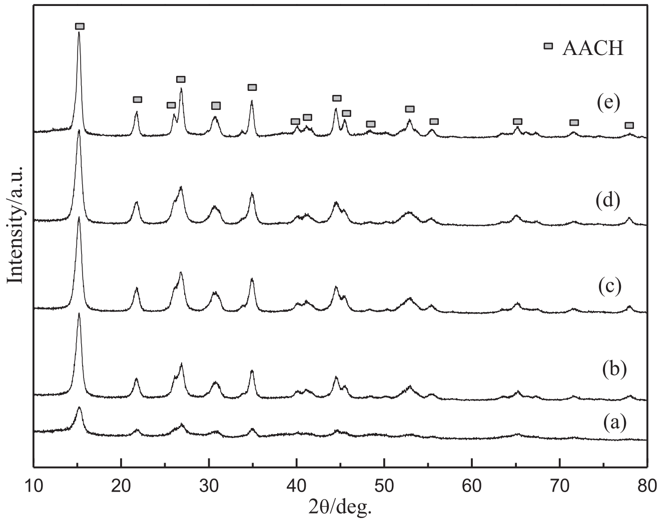

Fig. 2. XRD patterns of the precursors obtained at different pH values: (a) pH = 8, (b) pH = 8.5, (c) pH = 9, (d) pH = 9.5, (e) pH = 10.