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Novel eco-friendly method for preparation of mesoporous alumina from the product of rapid thermal treatment of gibbsite

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ABSTRACT

Novel eco-friendly method for preparation of mesoporous alumina from the product of rapid thermal treatment of gibbsite (CTA product) without "reprecipitation" stage is described. Compared with the nitrate-ammonia technology of "reprecipitation" of gibbsite to boehmite and its further calcination to γ-Al_2O_3, the new method consumed less amount of HNO_3 per 1 kg of Al_2O_3 (by 30 times), while the amount of effluents is twice lower. Effluents do not contain ammonium nitrate, since the preparation of boehmite does not include ammonia. It is shown that the method makes it possible to obtain boehmite with needle-shaped particle morphology. The particle size of boehmite and the textural characteristics of alumina are easily adjusted over a wide range by changing the temperature, aging time or peptizing agent. Thus, the pore volume of alumina may be 0.45–0.95 cm^3/g with an average pore diameter of 81–256 Å and S_{BET} = 140–240 m^2/g.

1. Introduction

Monohydrates of alumina with the structure of boehmite (pseudoboehmite) and the general formula AlO(OH)·nH_2O (где n = 0–1,0) are precursors of γ-Al_2O_3 that causes their wide application for preparation of alumina adsorbents [1], catalysts for the dehydration of ethanol to ethylene, catalysts of Claus process and etc. [2–5] and supports for catalysts of nitrous oxide production by oxidation of ammonia with oxygen, by oxidation of carbon monoxide, etc. [6].

Depending on the conditions of synthesis, boehmites strongly differ from each other in the morphology of the particles. There are three forms of boehmite particles: 1. needle-shaped particles, which crystallization occurs only in the direction of one axis; 2. rhombohedral plates, which are characterized by uniform growth along all axes; 3. "boats" and chains of "boats" [7]. To designate poorly crystallized boehmite, a special term "pseudoboehmite" was introduced [8]. The main differences of pseudoboemite from boehmite are the following: 1. The presence of the surplus water molecules in pseudoboehmite structure comparing to boehmite stoichiometry, which can be found both on the surface of the particles and in the interlayer space of the laminated "boehmite" structure [9]; 2. the smaller size of crystallites [10]; 3. the reduced temperature of the decomposition of aluminum hydroxide to γ-Al_2O_3 [11] that is caused by the increase in the length of hydrogen bond between layers, which in turn depends on the size of the crystallites [12].

Most of the world's boehmites are produced using technologies such as hydrolysis of alcoholates [7] and precipitation ("re-precipitation") [6], which allow regulation of physical and chemical properties of alumina over a wide range [13].

Boehmites prepared by hydrolysis of alcoholates are extremely expensive due to the use of alcohol and metallic aluminum.

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Besides, alumina supports with high purification degree is not necessary for catalysts preparation in most cases. Therefore, reprecipitation technology is more preferable, since in this case, the available reagents are used, and the synthesized boehmite is sufficiently pure.

Boehmites prepared by reprecipitation are characterized by needle (fibrous) and needle-plane particle morphology [14–17]. After calcination of these boemites, γ-Al_2O_3 with a high specific surface area ($>200\ m^2/g$) and a large volume of mesopores ($>0{,}4\ cm^3/g$), and also high mechanical strength of granules formed from monohydrate alumina [14].

According to the nitrate-ammonia scheme, reprecipitation of gibbsite includes the following reactions:

$$Al(OH)_3 + 3HNO_3 \rightarrow Al(NO_3)_3 + 3H_2O$$

$$Al(NO_3)_3 + 3NH_4OH \rightarrow AlO(OH)\downarrow + 3NH_4NO_3 + H_2O.$$

The scheme shows that it is necessary to use 6 mol of nitric acid and aqueous ammonia per mole of alumina ($2AlO(OH) \rightarrow \gamma$-$Al_2O_3 + H_2O$). Thus, when washing freshly precipitated boehmite from ammonium nitrate and other impurities in large quantities, chemically contaminated effluents are formed.

In this regard, there has been a significant interest in eco-friendly and resource-saving technologies. CTA (centrifugal thermal activation) technology can be refer to such technologies. CTA technology allow preparation of boehmite in mild conditions from the product of rapid thermal treatment of gibbsite (CTA product) without reprecipitation stage [18]. CTA product is prepared by rapid thermal treatment of gibbsite, also known as flash calcination of the one, in a centrifugal drum reactor of TSEFLAR™. Duration of the process is 1–3 s, temperature is 550–650°C. Unlike initial gibbsite, CTA-product with general formula $Al_2O_3{\cdot}nH_2O$ (где $n = 0{,}2$–$0{,}3$) is characterized by metastable intermediate structure, presence of 4, 5 and 6 oxygen coordinated aluminum cations, and high specific surface area (up to $250\ m^2/g$) [19]. These parameters cause its high activity when interacting with electrolytes and the ability to hydrate to boehmite or bayerite [20]. However, pore volume of alumina prepared from such boehmite does not exceed $0{,}4\ cm^3/g$ [21], that is insufficient for synthesis of the most catalysts containing alumina. It can be assumed that more "strict" hydration conditions under hydrothermal conditions will allow the control of textural properties of alumina, which is obtained by rapid thermal treatment of gibbsite, in a wider range.

The purpose of this work is to present a new eco-friendly and resource-saving method for preparation of mesoporous alumina with large pore volume from CTA product without reprecipitation stage. In addition, the influence of hydrothermal aging parameters of the preliminary hydrated CTA product on properties of the produced boehmite and alumina on its basis has been studied.

2. Experimental

2.1. Boehmite preparation

CTA-product obtained by rapid heat treatment of gibbsite in a centrifugal drum reactor TSEFLAR™ [20] was used as the starting material for the synthesis of aluminum monohydrates. The phase composition of the product according to the data of thermal and X-ray phase analysis is the following: 10% of boehmite, 90% of disordered χ-like Al_2O_3. The mass loss under calcination (1000 °C) is 5.7%. Textural characteristics: a specific surface area (BET) – $230\ m^2/g$, a pore volume (N_2) – $0.18\ cm^3/g$, an average pore diameter – 32 Å. The average volume diameter of the particles is 24 ìm.

Monohydrates of alumina were prepared in the following order:

1) Hydration of CTA-product in "mild" conditions in a solution of nitric acid with an acid module of 0.04 (mol HNO_3/mol Al_2O_3), T = 50 °C, solid to liquid ratio 1:5 and duration 2 h;
2) Washing the hydrated product of CTA with distilled water from impurities of Na;
3) Separation of the liquid and solid phases on the nutch-filter;
4) Hydrothermal treatment of the filter cake in a solution of nitric acid in a Parr 4520 autoclave with a volume of 2 L (USA, Parr Instrument Company);
5) Spray drying of the colloidal solution containing alumina monohydrate in YC-015 dryer (China, Pilotech) at an air outlet temperature of 130–150 °C.

Table 1
Conditions of hydrothermal treatment of hydrated and washed CTA-product.

Sample	Heating rate, grad/h	pH of the suspension	Content of Al_2O_3, %	Hydrothermal treatment temperature, °C	Aging time, h
Series 1					
1	25	1,4	10	150	6
2					8
3					10
4					60
Series 2					
5	10	1,4	10	140	24
6				150	
7				160	