Synthesis of Oxide Materials by Hydrothermal Hydrolysis of Aluminum Chloride Hexahydrate

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Abstract

In the present work, the processes of aluminum oxyhydroxides synthesis by hydrothermal hydrolysis in water solutions and in solid phase are considered. The process studies were conducted using a batch type autoclave at temperatures from 443 to 503 K at a pressure of 1.6 -2.3 MPa with the variation of such parameters as temperature, pressure, residence time of the reaction mixture in the reactor, flow velocity of the displacing gas during hydrolysis; number of washes, time and rate of hydrothermal decomposition products centrifugation, time and temperature of aluminium hydroxide drying. It is shown that Al-O-H product formed by hydrothermal hydrolysis of aluminum chloride hexahydrate $AlCl_3$* 6 H_2O, and urea jointly in water solutions is a highly dispersed (nano) γ-AlOOH (boehmite). Hydrothermal process of self-hydrolysis of aluminum chloride hexahydrate in solid phase with the use of crystalline water is lead to formation of bayerite (mainly) and aluminum oxychlorides with a total Cl content of not more than 4 %.

Keywords: alumina production, hydrolysis, hydrothermal synthesis, bayerite, boehmite.

1. Introduction

Currently, for the production of alumina from high-silicon raw materials, mainly kaolin, alkaline technologies are widely used. The proposed promising technologies are based on acidic methods for processing of kaolins and clays use sulfuric, hydrochloric and nitric acids, but they are multistage and high-cost [1].

The most advanced technology includes the leaching of raw materials with a solution of hydrochloric acid in an autoclave, separation of the resulting pulp, crystallization of aluminum chloride hexahydrate from clarified aluminum chloride solution with gaseous hydrogen chloride, calcining aluminum chloride hexahydrate to produce gamma-alumina and its final recrystallization in alkali solution to obtain metallurgical grade alumina. However, this technology can be significantly simplified by replacing the operations of crystallization and calcination of aluminum chloride hexahydrate by the decomposition operation to obtain aluminum hydroxide, which is directed to alkaline recrystallization. The method of hydrothermal hydrolysis of aluminum chloride hexahydrate is most suitable for replacing the existing energy-consuming multi-stage high-temperature methods of aluminum chloride decomposition [2].

The advantages of the hydrothermal hydrolysis method of producing Al-O-H products are:
1. Single-stage process;
2. Low energy consumption;
3. Chemical and phase purity of the product;
4. Low level of aggregation;
5. The ability to control the size, morphology and structure of the obtained Al-O-H products;
6. The possibility of using this method for high-silica raw materials of various origin.

Important features of the hydrolysis of aluminum chlorides in solutions at elevated temperatures (373-773 K) are [3]:
(a) The incompleteness of the second and third hydrolysis steps;
(b) The formation of soluble multicore aluminum oxychloride complexes forming colloidal solutions;
(c) The strong dependence of the hydrolysis depth on the acidity of the medium and on the presence of additional components in the solution.

Based on the literature data, boehmite (or its modification - pseudo-boehmite) is the only Al-O-H product that can be obtained under mentioned hydrothermal conditions (temperature 433-513 K and pressure 0.6-2.4 MPa) in the presence of additional components that enhance hydrolysis. The output of boehmite is a quantitative estimate of the depth of hydrolysis of aluminum chloride. 100 % yield of boehmite indicates complete hydrolysis of aluminum chloride [4].

At the same time, there are no data about the possibility of hydrothermal hydrolysis with the production of Al-O-H products from crystalline aluminum chloride hexahydrate in solid phase—that is, in the process of self-hydrolysis involving lattice water of the crystalline hydrate.

The purpose of this work was to determine the possibility of carrying out the process of complete hydrolysis of aluminum chloride hexahydrate at elevated pressures and temperatures under hydrothermal conditions with the production of alumina products.

2. Experimental

The hydrolysis in water phase was performed under hydrothermal conditions with aqueous solutions of $AlCl_3 \cdot 6H_2O$ (analytical grade with ≥ 98 % purity) with concentration of 3.0–30.0 wt. %., which was obtained from commercial source and used without purification. Carbamide of analytically pure grade with concentration of 8.5 – 20.2 wt % was served as an additive accelerating the hydrolysis. The solution volume was 30–60 mL. Experiments were performed at a temperature of 160 – 200 °C and pressure of 0.6–1.6 MPa in a 200-mL autoclave reactor, which was a part of the laboratory experimental setup, described early [5].

The characteristics of the installation enabled experiments on hydrothermal hydrolysis at temperatures of 423 ‑ 523K and pressures of 0.1 ‑ 5.0 MPa, with the measurement error and parameter adjustment accuracy of no worse than 3 % under the conditions of an inert gas flowing through the reactor. The pressure in the system was provided by the flow of argon delivered to the reactor inlet and varied with upstream and downstream high-pressure gas controllers, with the pressure corresponding to the saturated water vapor pressure at the prescribed temperature of experiment.

The reactor outlet was connected to a trap filled with distilled water to catch gaseous products carried away by the flow of argon. The argon flow rate was maintained constant and equal to 0.00125 $m^3 h^{-1}$. The experiment duration was 1 to 10 h.

The resulting insoluble hydrolysis products were washed several times with distilled water, with the subsequent centrifugation of the sediment. The centrifugation was performed in the course of 8 min at a rotor speed of 2600 rpm. Further, the washed samples were dried at T = 353 K for 5 h. The composition and content of the insoluble precipitate was determined by weighing, X-ray fluorescence method, X-ray diffraction (XRD) analyses and ^{27}Al MAS NMR.

The complete hydrolysis of $AlCl_3$ occurs at a ratio $AlCl_3/(NH_2)_2CO$= 0.67 at a temperature of 433-513 K and a pressure of 0.6 - 2.4 MPa in aqueous solutions with the yield of 100 % a highly dispersed γ-AlOOH (boehmite).

The possibility of hydrothermal self-hydrolysis of aluminum chloride hexahydrate with the removal of HCl from the reaction zone to produce bayerite was established for the first time. The most effective process of self-hydrolysis takes place at a temperature of 513 K and a pressure of 1.5 MPa. While bayerite is the main product of the self-hydrolysis of $AlCl_3 \cdot 6H_2O$ in solid phase.

In all cases, the total content of Cl in the products of hydrolysis does not exceed 4 % wt.

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6. References

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