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Reactions analysis during the synthesis of pseudo-boehmite as precursor of gamma-alumina

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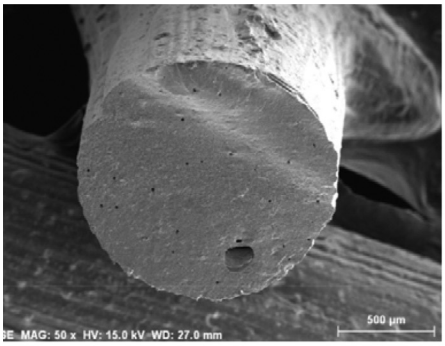
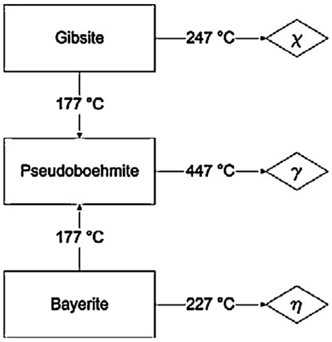
ABSTRACT

Pseudo-boehmite is the best precursor during synthesis of gamma alumina, because only the removal of water by calcination at about 447 °C is required. The control of operating variables during synthesis of pseudo-boehmite: the supersaturation of the solutions is a factor of special importance, additionally the pH, temperature, impurities and nature of the reagents [3,4]. Ensure purity of this material and these variables determine the morphology, texture and it structures of the precipitate. Therefore, it is relevant to follow phenomena that occur during synthesis, in order to predict yield and quality of the final product. In this work, synthesis of pseudo-boehmite was developed by the method of precipitation, using industrial grade aluminum sulfate supersaturated solution and concentrated ammonium hydroxide (28%) as reactants; this known method was improved decreasing reaction temperature below the boiling point of ammonia. Temperature control of the reactant medium was reached by data acquisition and automatic manipulation of the heating medium. It is shown that operating the reactor at isothermal conditions ensures the final quality of the pseudo-boehmite produced.



Gamma alumina extrudate .



Sequence dehydration.

1. Introduction

It has been pointed out that pseudo-boehmite, which exhibits poor crystallinity compared to the boehmite phase, is the precursor that requires less energy for the synthesis of nanometric γ-alumina; therefore, it could be a useful raw material during preparation of γ-alumina [6]. Synthesis of pseudo-boehmite can be carried out using aluminum sulfate and ammonium hydroxide, in an aqueous phase reaction system. Reacting conditions such as pH, reactants concentration and temperature could induce formation of γ-$AlO(OH)_3$ (gibsite) and α-$Al(OH)_3$ (bayerite); higher temperatures favor formation of dehydrated forms such as α-AlO(OH) (diaspore) and γ-AlO(OH) (boehmite), the desired product. Nevertheless, if temperature is high enough to boil the ammonium, b.p. = 57 °C, derived from ammonium hydroxide, synthesis procedure becomes complicate because of lack of control of pH. This lack

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Notation

Substances

$A.$ – $Al_2(SO_4)_3$ aluminum sulfate
$B.$ – NH_4OH ammonium hydroxide
$C.$ – $(NH_4)_2SO_4$ ammonium sulfate
$D.$ – $Al(OH)_3$ aluminum III hydroxide
$E.$ – AlO_2^- aluminate ion
$F.$ – H_2O water

Model variables

C_j	concentration of the jth compound, mole/cm^3.
F_j	volumetric flow of the jth compound, mL/s.
K_b	equilibrium constant for dissociation of ammonium hydroxide, cm^3/mole.
k_K	reaction rate constant for the kth reaction, cm^3/s mole.
K_k	equilibrium constant for the kth reaction, consistent dimensions.
V_R	reactor volume, mL.
$\in_k$	molar advance of the kth reaction, mole/s.
θ	molar fraction of dissociated ammonium hydroxide, dimensionless.
ΔH_{r_k}	heat of the kth reaction, kJ/mole.

Sub-index

i	initial conditions.

of control reduces the yield to desired products as well as quality of them; therefore it is important to control operating variables in order to obtain pseudo-boehmite as main product, because it will confer properties such as porosity and mechanical resistance to the γ-alumina obtained after calcination at 500 °C. The original synthesis method by [6] proposed reaction at 70 °C, which is over the boiling point of ammonium. In this work this synthesis temperature is regulated at 50 °C in order to avoid the evaporation of ammonium, which means loss of one important reactant and lack of ability to control the pH changes during reaction.

Two main reactions have been identified during synthesis of pseudo-boehmite from aluminum sulfate and ammonium hydroxide [4]:

(1) formation of aluminum (III) hydroxide, ΔH_{r_1} 28.15 kcal/mol (Eq. (1)).
(2) its transformation into pseudo-aluminum (III) oxide, ΔH_{r_2} 37.24 kcal/mol (Eq. (2)).

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 3(NH_4)_2SO_4 + 2Al(OH)_3 \quad (1)$$

$$Al(OH)_3 + OH^- \Leftrightarrow AlO_2^- + 2H_2O \quad (2)$$

In this work, synthesis conditions to obtain pseudo-boehmite as main product are found; and discussion about temperature and pH effect is given by inferring formation of materials and their development along reaction time.

2. Materials and methods

2.1. Experimental devices

Pseudo-boehmite synthesis took place in a 1000 mL batch stirred reactor (Fig. 1) equipped with a pH sensor, a RTD and two reactant dispensers (for aluminum sulfate and ammonium hydroxide). Supply of ammonium hydroxide was used as the manipulate variable that controls pH [3]; the added amount of this reactant was used to follow the two main reactions, by combining energy and mass balances in the reactor. Reactor temperature was controlled by manipulating heating duty of the heating medium and addition of ammonium hydroxide at room temperature.

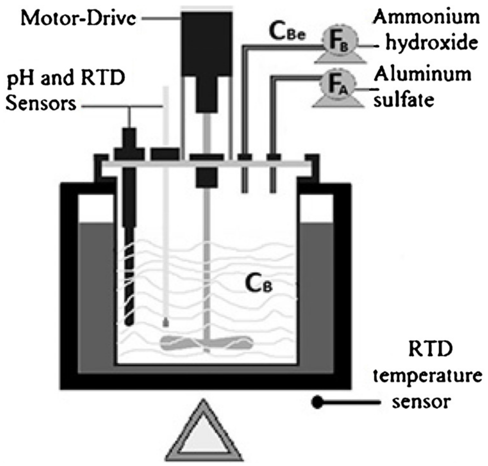

Fig. 1. Semi-batch reactor and instrumentation.

Preparation of pseudo-boehmite is started loading the reactor with 150 mL of concentrate ammonium hydroxide (Golden Bell, 28%); initial concentration is estimated as $C_{Bi} = 66.82$ M. This aqueous solution is heated up to 50 °C by means of hot water supplied to the heating medium. Then a constant flow of 120 mL/h of aluminum sulfate, industrial degree, at concentration $C_{Ai} = 0.33$ M = 0.113 g/mL, is fed to the reactor, in order to start the reactions (Eqs. (1) and (2)). During this addition, temperature of the heating medium is adjusted in order to control reaction temperature at 50 °C. After 1200 s it is observed that temperature stabilizes by itself, then another shot of 150 mL of concentrate ammonium hydroxide is supplied to the reactor and the cycle is repeated. This process continue until the volume of reacting solution reaches $V_R = 1.0$ L, controlling the temperature inside the reactor at 50 °C and recording temperatures of heating medium at intervals of 0.1 s.

2.2. Stoichiometry and equilibrium constants

Concentration of ammonium and hydroxyl ions were estimated from pH measures along the reaction time [3,4]. For this purpose, the dissociated fraction of ammonium hydroxide (Eq. (3)) as well as its equilibrium constant (Eq. (4)) was evaluated.

$$\frac{NH_4OH}{C_{Bi}(1-\theta)} \Leftrightarrow \frac{NH_4^+}{C_{Bi}\theta} + \frac{OH^-}{C_{Bi}\theta} \quad (3)$$

$$K_b = \frac{[C_{Bi}\theta]^2}{[C_{Bi}(1-\theta)] \cdot V_R} \quad (4)$$

Now, Eq. (4) can be solved for the initial concentration of ammonium sulfate (Eq. (5)). Then the value of hydroxyl concentration can be obtained (Eq. (6)), which is related with the pOH of the reacting solution (Eq. (7)). Finally, combining relationship between pH and pOH (Eq. (8)), it is possible to find the equilibrium constant of dissociation with the initial conditions of the reacting solution, by solving intrinsically (Eq. (9)).

$$(C_{Bi}\theta)^2 + K_b V_R (CB_i\theta) - K_b V_R CB_i = 0 \quad (5)$$

$$[OH^-] = C_{Bi}\theta \quad (6)$$

$$pOH = -\log(C_{Bi}\theta) \quad (7)$$

$$pH = 14 + \log(C_{Bi}\theta) \quad (8)$$