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Effect of precipitation process parameters on boehmite properties: In situ optical monitoring

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HIGHLIGHTS

- Boehmite is precipitated either in double-jet stirred tank reactor or micro-mixer.
- Supersaturation would be the major parameter which controls aggregation.
- Multiple light scattering brings out differences during precipitation.

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ABSTRACT

Alumina, which is a catalyst support, is obtained by boehmite calcination. This work aims to study boehmite precipitation and the impact of this step on alumina quality. Precipitation of boehmite is studied in a double-jet stirred tank and with a micro-mixer. These devices induce different mixing of the reagents and different evolution of the supersaturation. Precipitation is followed on-line with an optical apparatus based on multiple light scattering. Alumina obtained with micro-mixer presents significantly lower specific surface area, pore volume and mean pore diameter than the one obtained with the double jet reactor, showing a totally different crystallite aggregation. Using different types of micromixers at isosupersaturation, the results show that Reynolds number in the micro-mixer, stirring power in the receiving vessel and micro-mixer type have no effect on porosity and thus on aggregation, which could be explained by a supersaturation that is sufficiently high to prevent other parameters from having effects. Using double jet reactor, feeding time directly affects initial supersaturation, which level is lower than the one created in micro-mixer. For double jet precipitation, the textural properties are directly correlated to the initial supersaturation. Alumina obtained with the highest value of supersaturation with double-jet stirred tank has similar porosity value than the one obtained in micro-mixer. This supersaturation level would thus be a threshold beyond which other operating parameters have no effect. Aggregation would be directly controlled by initial supersaturation. Furthermore, it was shown that differences of alumina textures are correlated with different behaviors of backscattering levels. This technique allows the in situ characterization of aggregation differences, during precipitation, before the impact of filtration–washing–drying steps on aggregation.

1. Introduction

γ-Alumina is a catalyst support Al_2O_3, used in many refinery processes. This material is obtained from calcination of boehmite AlOOH. Transformation of boehmite to γ-alumina is topotactic [1,2], with the morphological properties of boehmite being largely preserved during the phase change. The control of alumina properties, and therefore of boehmite, is essential to optimize the catalysts.

Various synthesis routes are possible for boehmite. It can be prepared by the sol gel process using aluminum alkoxides [3,4]. However, the synthetic route used industrially involves the precipitation of aluminum salts, which may be followed by a period of ripening in hydrothermal conditions [5–7].

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Several aluminum salts can be used to obtain boehmite, such as aluminum nitrate, $Al(NO_3)_3$ [8–10], aluminum chloride, $AlCl_3$ [8], or aluminum sulfate, $Al_2(SO_4)_3$ [8,11]. The latter reagent was used in this work. Sulfate ions have huge importance since they direct aggregation. Sulfate ions are bound by hydrogen bonds, in acidic conditions [11], since they have high affinity for aluminum [8]. This adsorption would be selective, on [010] and [001] faces [11]. Thus, the growth of boehmite would occur preferentially on [100] faces, resulting in the formation of fibrillar boehmite [7].

The effects of physicochemical conditions on boehmite precipitation are relatively well known. Temperature and pH are the most influential parameters [9,10,12], and to a lesser extent, the reagents [7,8].

Nevertheless, little work concerns the mechanisms managing crystallites formation and their aggregation, which is the source of the porosity of the material. Rousseaux et al. [13] studied the effect of different precipitators on boehmite particle properties, and, in particular, the effect of operating parameters. These authors show that increasing the intensity of vessel mixing decreases the crystallite size. They also show that using two different technologies of reactors (vortex reactor and sliding surface reactor) and varying the profiles of the suspension circulation inside the reactor, i.e. the way the existing particles go through the reaction zone where fresh reagents are introduced, the porous volume and mean pore diameter change. Another work has shown that using sliding surface mixing device, whose mixing is more efficient than in vortex reactor, gives higher specific surface area, porous volume and mean pore diameter [14]. Effect of mixing on gibbsite precipitation has been studied. Ilievski et al. [15] showed that gibbsite agglomeration is affected by shear rate, which is expected to have an effect on particle capture efficiency. Mixing, which is expected to control collision rates, has not a significant effect on precipitation, in the case of gibbsite.

Another aspect of boehmite precipitation is to obtained in situ data without disturbing the suspension structure by sampling. Recently, direct techniques were developed to characterise on-line and in-line properties of concentrated dispersions in a non-intrusive and non-denaturing way.

Raman spectroscopy [16], which allowed quantifying the impact of mixing rate or seeding parameters [17], chemical imaging [18], FTIR [19] which is a supersaturation sensor, X-ray diffraction [20], FBRM [21] which has given information about the influence of process conditions on the formed material, ultrasonic attenuation spectroscopy [22]. Ultrasonic spectrometry techniques for example, provide advantages for on-line particle size analyses, particularly the ability to operate on undiluted and optically opaque media. The technique consists in propagating ultrasonic waves of variable frequency through the particulate system and measuring the frequency dependence of the attenuation to derive particle size [23–26]. The ultrasonic velocity method and the electroacoustic technique can also be used for particle size characterization in concentrated systems. The ultrasonic velocity method consists in measuring the transit time of pulsed multiple frequency ultrasonic waves propagating through a medium [27]. In the electroacoustic method, an alternating electric field causes the electrically charged particles to move back and forth generating sound waves. Zeta potential and particle size are derived from the analysis of sound waves in relation with particle motions [28].

Multiple light scattering methods represent an alternative to acoustic spectrometry techniques for the characterization of particles flows. In the multiple scattering regime, the transport mean free path representative of particle size indeed can be derived from the analysis of the light flux distribution in the incoherent backscattered spot light [29–31]. In a previous works, the multiple light scattered was analysed from a concentrated dispersion (Turbiscan On Line instrument) during calcium carbonate batch precipitation. Size and mean refractive index of particles or nuclei agglomerates are derived from measurements of the backscattered light flux on the basis of a multiple light scattering model [31,32].

Our study focuses on understanding the impact of precipitation processes and process parameters on the aggregation of boehmite crystallites, and the effect on material quality, by following precipitation with the on-line optical device Turbiscan On Line. In this study, precipitation experiments in double-jet stirred tank reactor and with a pre-mixing device were compared. The effect of the addition time of the whole reactants and of the mixing, on material properties were analyzed.

2. Materials and methods

2.1. Precipitation–reaction

Boehmite is synthesized by mixing an aluminum sulfate solution with a sodium aluminate solution through the heterogeneous reaction:

$$Al_2(SO_4)_{3_{(aq)}} + 6NaAl(OH)_{4_{(aq)}} \rightarrow 8AlOOH_{(s)} + 3Na_2SO_{4_{(aq)}} + 8H_2O \quad (1)$$

All chemicals involved in this synthesis were reagent grade and used as received without further purification. pH was controlled at 9 and temperature was 60 °C.

After synthesis, the suspension was filtered and washed five times with water ($T = 60$ °C) in order to minimize the content of impurities (Na^+ and SO_4^{2-}). The cake was dried at 120 °C overnight and then ground. Dry boehmite was finally calcined during 4 h at 540 °C in order to obtain γ-alumina (γ-Al_2O_3).

2.2. Precipitation set-up

In this study, experiments were carried out in a 2 L stirred tank reactor with two types of mixing systems: double-jet of the reagents in the stirred tank or pre-mixing of the reagents before introduction in the stirred tank.

2.2.1. Double-jet stirred tank reactor

Aluminum sulfate solution ($Al_2(SO_4)_3$) ($C = 0.35$ mol/l, $V = 175$ ml) was introduced simultaneously with a sodium aluminate solution ($NaAl(OH)_4$) ($C = 0.99$ mol/L, $V = 262$ ml), over 30 min, in a stirred vessel containing water (660 ml) at constant conditions of temperature and pH (60 °C and pH = 9). Water was also added during precipitation ($V = 903$ ml). The molar ratio $R = n_{NaAl(OH)_4}/n_{Al_2(SO_4)_3}$ was equal to 4.2. All these conditions were fixed in order to obtain predominantly boehmite (and no gibbsite or other polymorphs). A pH regulation maintained the pH at 9 by controlling a sodium aluminate solution pump (Fig. 1). Suspension was analyzed throughout the precipitation with an on-line optical device (Turbiscan On Line instrument) (see Section 2.3) using a peristaltic pump.

The reactor was a standard cylindrical stirred tank equipped with an 8 cm 4-blade Teflon-coated impeller. Four baffles prevented vortex formation. Mixing parameters are shown in Table 1.

In the stirred tank reactor mixing inhomogeneity due high reagent feed rates and volume variation, results in inhomogeneity of supersaturation, due to gradients of solution [33] and particle concentration [34] and having an effect on primary nucleation [35].

In fact, the variation of supersaturation is due to the progressive addition of the reagents over 30 min, inside the vessel containing a suspension changing spatially because the concentration is not homogeneous in the tank, and temporally, since, according to the progress of the reaction, the particles are formed in an already