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High Energy Milling of Boehmite: Changes in Particulate Characteristics

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Abstract

Changes in particulate characteristics of boehmite during high energy milling/ mechanical activation (MA) carried out in a planetary mill is the theme of this paper. Boehmite used in the study, prepared by thermal dehydroxylation of gibbsite, has been characterized by a monomodal size distribution with a median size (d_{50}) of 110 mm, and large BET specific surface area (264 m^2/g). Keeping other parameters constant, the extent of activation has been varied by changing the milling time (0 to 240 min). High impact forces prevailing in the mill has resulted in changes in the particulate characteristics such as size reduction, changes in specific surface area etc, and structural disordering. With the progress of milling, size reduction ceases and particle aggregation sets in. BET specific surface area has anomalously decreased during milling. Analysis of such changes during MA is described in this paper.

Keywords: boehmite, mechanical activation, particulate characteristics, specific surface area, pore size distribution

1. Introduction

Bayer process of alumina production continues to remain unchallenged since its inception, over more than a century ago. In this process, aluminium minerals (gibbsite [ã-Al(OH)$_3$], boehmite [ã-AlOOH] and diaspore [á-AlOOH]) in bauxite ore are selectively digested in hot concentrated caustic solution in the first step, leaving other associated minerals in the residue. Less reactive monohydrates need higher temperature and alkali concentration for their dissolution; equation (1) represents the dissolution of boehmite:

$$\gamma - AlOOH_{(s)} + NaOH_{(aq)} \rightarrow Na^{+} Al(OH)_{4}^{-1}{}_{(aq)} \quad (1)$$

High energy milling of monohydrate minerals of Al are being tried to enhance their reactivity, and thereby increasing its leachability in caustic solution (Pawlek et al., 1992, Taskin et al., 2009). Changes in particulate characteristics, which influence the reactivity of materials during high energy milling, are generally not

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highlighted. This paper specifically focuses on the changes in particulate characteristics of a high surface area boehmite during high energy ball milling.

2. Materials and Methods

2.1. Boehmite

Details of the preparation and characterization of boehmite used in this study have been reported earlier [Alex et al., 2013]. Detailed characterisation using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and thermal analysis studies has shown that the test sample is phase-pure boehmite.

2.2. Mechanical Activation

A batch type planetary mill (Pulverisette P6, Fritsch GmbH, Germany) has been used for mechanical activation (MA). Milling conditions are: ball to powder ratio =30:1, rotational speed =400 rpm, milling time 0-240 min.

2.3.Characterization

Particle size distributions (PSD) of milled and unmilled boehmite samples have been determined using a particle size analyzer based on laser diffraction (Model: Mastersizer, Malvern, UK). Micromeritics ASAP2020 surface area analyser has been used to measure the BET specific surface area and pore size distributions. Geometric specific surface area has been deduced from the PSD distribution. Morphological features are studied using a scanning electron microscope (SEM) (Model: 840A, Hitachi, Japan).

3. Results and Discussions

3.3. Boehmite used

Boehmite used in this study has been found to have a monomodal distribution with a median size, d_{50} of 110 mm. Other characteristic diameters, d_{10} and d_{90} are 77 mm and 153 mm, respectively. Geometric specific surface area deduced from the PSD is ~0.1 m^2/g. BET specific surface area, on the other hand, has been found to be exceptionally large, ~264 m^2/g compared to that reported in many studies (~1 m^2/g). Such a large difference is attributed to the difference in the preparation process. Most of the low surface area boehmites described in earlier studies have been prepared by hydrothermal methods whereas boehmite used in this study has been prepared by thermal decomposition of gibbsite. Constitutional water released during thermal decomposition of gibbsite creates large number of slit shaped pores, as shown in Fig. 1, for their exit and thereby resulting in a highly porous boehmite. XRD (JCPDS No. 83-2384) and FTIR studies have shown that the synthesized material is phase pure boehmite.

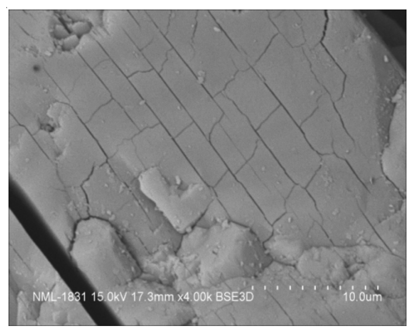

Fig. 1: SEM micrographs of boehmite showing slit like pores on the surface

2.3. Particle size distribution of milled boehmite

Particle size data of milled boehmite obtained from the sizer are presented in Fig. 2 in terms of reduction ratio of median size; i.e. the ratio of median size at any milling time, $d_{(50,\ t)}$ and median size of unmilled sample, $d_{(50,0)}$ is plotted as a function of milling time. High milling efficiency of planetary milling is evident in Fig. 2; particle size (median size) shows ~60 times reduction in just 15 min of milling. Beyond 15 min of milling, however, the reduction ratio is seen to increase, indicating coarsening of particles; such coarsening is ensuing from particle aggregation on account of the intense particle-particle interactions. During high energy milling, especially in dry operations, such aggregation/agglomeration is quite possible (Juhasz and Opoczky, 1990).

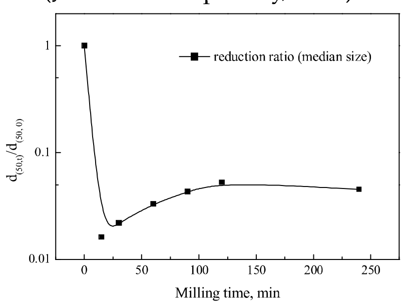

Fig. 2: Variation of size reduction ratio of with milling time

3.5. Specific surface area and pore size

Geometric specific surface area of boehmite milled for different durations of time along with that of unmilled sample is presented in Table-1.There is an initial increase followed by a decrease, a trend just reverse that of particle size reduction as it an inverse function of PSD. BET specific surface area of milled boehmite is also included in Table-1 to have a comparison with the geometric specific surface area. BET specific surface area, as shown in Table -1, has continuously decreased with milling time instead of a typical increase with decrease in particle size; such a significant reduction in specific surface area cannot be accounted by particle aggregation alone, inferred from particle size analysis data (Fig. 2).

Table 1: Variation of specific surface area of boehmite with milling time

Milling time, min	Specific surface area, m²/g	
	Geometric	BET
0	0.1	264.1
15	2.7	201.2
30	2.6	188.9
60	2.4	143.1
120	2.2	115.1
240	2.1	67.6

To understand the anomalous decrease in specific surface area, various milled samples have been characterised in terms of N_2 adsorption at liquid N_2 temperature. Nature of adsorption isotherms (not shown here) has been found to be different for the milled sample; such changes reflect changes in the pore characteristics. Detailed analysis of these adsorption isotherms has been carried out using BJH method (Barret et al., 1951). Pore size distributions of milled samples and unmilled samples estimated by BJH method are presented as cumulative distribution in Fig. 3. It can be seen that majority of the surface area of unmilled boehmite is from micropores having size < 5 nm. The average pore diameter is found to be around 3 nm. As the milling progressed, a decrease in the pores having size < 5 nm and a consequent decrease in specific surface area is observed. Contribution of bigger pores towards surface area has, however, been noticed. Consequently, the average pore diameter has increased to ~13 nm after 240 min of milling. This indicates that the decrease in specific surface area during milling results mainly from the annihilation of pores having size < 5 nm.

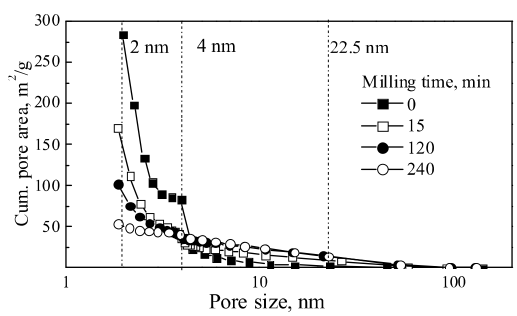

Fig. 3: Cumulative pore area of boehmite milled for different time

3.3. Morphological Features

To understand the extent of particle aggregation inferred from PSD and pore size analysis, changes in the morphological features under the influence of planetary milling have been studied using a SEM; SEM micrographs of particles milled for 3 min and 60 min and are presented in Fig. 4 (a) and Fig. 4(b), respectively. Disjointing of the platelets (of initial unmilled boehmite) occurs during early stages of milling. Images at higher magnification show smaller particles sticking to the larger particles even for 3 min milled samples as seen in Fig. 4(a). As the milling time is increased to 60 min, the smaller particle sticking to the bigger ones diminishes almost completely, and aggregation of smaller elongated particles is observed in the sample [Fig. 4(b)]. Such severe aggregation is responsible for the annihilation of micropores and decrease in specific surface area, in turn.

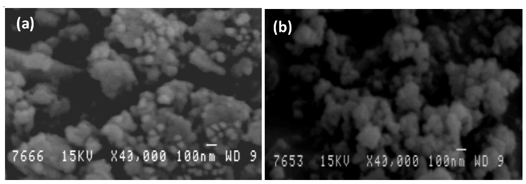

Fig. 4: SEM images of milled boehmite: (a) 3 min (b) 60 min

2.3. Reactivity

Reactivity, in general, is synonymous with specific surface area; it increases as the specific surface area increases while a decrease occurs when specific surface area decreases. In spite of the anomalous decrease in BET specific surface area, it is observed that that the reactivity of boehmite in terms of alkali dissolution and thermal transformation (details are not covered here) increases with the milling time. It is the structural changes such as increase in microstrain, decrease in microcrystallite dimension etc. (not detailed here) that are responsible for the enhanced the reactivity; structural changes offset (and surpass) the effect of 75% reduction in specific surface area.

3. Conclusions

Conclusions drawn from the study is summarised below:

- Sharp size reduction in early stages of planetary milling shows high milling efficiency
- Aggregation of particles as a result of particle-particle interactions
- Anomalous decrease in BET specific surface area of boehmite with milling time
- Changes in pore characteristics leads to the decrease in specific surface area
- Despite the anomalous decrease in specific surface area, reactivity increases with milling

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