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Original Research Paper

Study on the stability and microstructural properties of barium sulfate nanoparticles produced by nanomilling

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ABSTRACT

Barium sulfate nanoparticles were produced by nanomilling in stirred media mill using sodium salt of polyacrylic acid (PAA-Na) as a dispersant. The particles sizes of the ground product obtained in the grinding mill were determined by dynamic light scattering (DLS), Brunauer–Emmet–Teller (BET) nitrogen gas adsorption method, and transmission electron microscopy (TEM). The mean particle size calculated with various methods yielded different values due to the different characterization techniques. The stability of $BaSO_4$ nanoparticles produced was analyzed by zeta potential measurement and Turbiscan. The stability of barium sulfate nanoparticles was high in presence of dispersant PAA-Na and higher pH values. Further, the changes in microstructural properties, caused by wet grinding and adsorption of PAA-Na on $BaSO_4$ nanoparticles, were studied using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The surface activation and amorphization of $BaSO_4$ nanoparticles were observed due to increased stresses exerted on the particles during wet grinding.

1. Introduction

Nanomilling is a promising wet grinding technology for the production of nanoparticles to meet increasing demand for the advanced materials. Amongst different grinding mills stirred media mill is an important grinding device for the production of ultrafine materials effectively owing to ease of operation, simple construction, high size reduction rate and low wear contamination [1] and have been used extensively in many industries where a high product fineness is demanded, viz., paints, pigments, papers and plastics, ceramics, rubber, minerals, coal, chemicals and pharmaceuticals, agrochemistry, food, bioengineering and nanotechnology [2]. Nanomilling in a stirred media mills have many advantages like reduced agglomeration tendency compared to dry grinding; material losses are avoided; no dust explosions and oxidations; easier handling of toxic materials; no devices for air cleaning required; improvement of heat transfer [3]. The production of submicron and nanosized particles of different materials in stirred media mill was reported widely in the literature [4–9]. Main issue concerning the nanoparticles production by nanomilling is stabilization of nanoparticles since they have increasing tendency of aggregation due to the effects of electrostatic and Van der Waals interparticle forces as the size reduces below 100 nm [10]. An increase in interparticle interactions with decreasing particle size causes agglomeration of particles. Also an increase in the viscosity and occurrence of yield stress of the product suspension is observed with progress of grinding due to attractive interparticle interactions [11]. Thus, an appropriate stabilization mechanism must be in place during nanomilling to ensure the smooth progress of process. Generally ultrafine particles are stabilized by electrostatic and steric or electrosteric stabilization. Electrostatic stabilization is effected by potential determining ion on particle surface. Steric stabilization involves addition of polymeric dispersant which adsorbs on the particle surface to act as barrier between the particles and prevent agglomeration [12].

Another interesting area in fine grinding process is the mechanochemical effects caused by structural distortions of crystalline materials during wet grinding. In addition to size reduction, the mechanochemical effects are caused on the particles surface due to the transfer of high energy by the grinding media [13]. The changes in structural properties may often results into advantageous properties such as reduction in sintering temperature, enhancement in pozzolanic reactivity of cement filler, nanocrystalline materials production, improvement in waste materials reactivity, strong enhancement of the catalytic properties of oxides, phase transformation, and generation of new phases [11,14,15]. Several studies regarding mechanical activation and structural changes were reported during stirred media milling. The mechanochemical change of alumina to alumina hydroxide was reported by

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Stenger et al. [11] during wet grinding. It is also reported that comminution of calcite, carbonate minerals, silica leads to a progressive loss in crystallinity of the crystalline materials reflected by peak intensity reduction and XRD line broadening [7,16]. The model substance used for the present study is barium sulfate. Barium sulfate is an important inorganic chemical product widely used on account of its high specific gravity, opaqueness to X-rays, inertness and whiteness [17]. Barium sulfate is used to achieve a high sun protecting factor in cosmetics, as packing material; additive in painting, varnishes, coating and plastics and barium sulfate nanoparticles will likely to be used in many applications [12,18].

The effects of dispersant PAA-Na and suspension pH on the stability of barium sulfate nanoparticles produced by nanomilling was investigated by zeta potential measurement and Turbiscan analysis in the present contribution. Particle size measurement was carried out using different characterization techniques; viz., dynamic light scattering (DLS), Brunauer–Emmet–Teller (BET) nitrogen gas adsorption method, and transmission electron microscopy (TEM). Further, the changes in structural and surface properties of barium sulfate nanoparticles caused by intensive grinding were investigated using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) techniques.

2. Materials and methods

2.1. Materials

Barium sulfate ($BaSO_4$) material used in this work was obtained from M/S. 20 Microns, Vadodara, India. The volume weighted mean ($d_{4,3}$) size of feed material is 11.18 μm with the specific surface area of 0.85 m^2/g. The particle size distribution of feed barium sulfate material was presented elsewhere [9]. The SEM image and energy-dispersive X-ray spectroscopy (EDS) analysis of feed barium sulfate is represented in Fig. 1 and Table 1 respectively. The sodium salt of polyacrylic acid, average molecular weight of 4000 g/mol, was used as a dispersant in the milling study. It is 20% by weight sodium salt of polyacrylic acid solution in water purchased from Himedia Laboratories, Mumbai, India. All the suspensions used in experiments were prepared in Millipore water (Millipore, Elix, Bangalore, India). The NaOH and HCl solutions used for pH adjustment were of analytical grade. The wear resistant cesium oxide-stabilized zirconia (ZrO_2) grinding beads (density of 6200 kg/m^3 and a chemical composition of 83% ZrO_2 and 17% CeO_2) with average size of 500 μm purchased from M/S. Jyoti Ceramics, Nasik, India, were used for the wet grinding experiments.

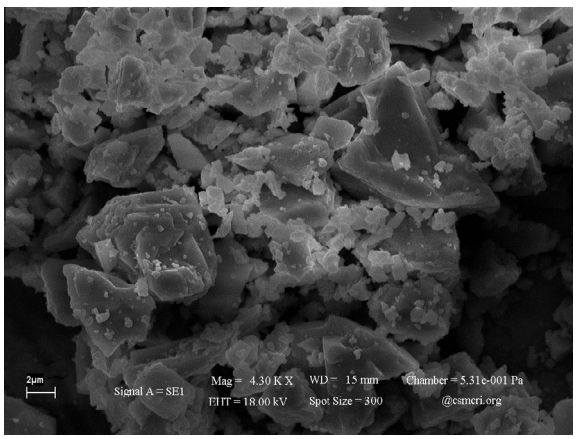

Fig. 1. SEM image of feed barium sulfate.

Table 1
Elemental analysis (EDAX data) of feed barium sulfate used in the study.

Elements	Weight %	Atomic %
O	26.62	64.22
Si	4.62	6.35
S	10.95	13.18
Ba	57.81	16.25

2.2. Experimentation

Vertical laboratory stirred media mill operating in batch mode was used to conduct grinding experiments as shown in Fig. 2. The mill consists of stainless steel vessel of 0.5 L capacity with cooling water jacket and a pin type stirrer with four cylindrical rods placed at right angles. The grinding media and suspension of powder prepared in the Millipore water are charged into the mill. Cooling water is supplied by circulating cooling water bath through the jacket of stirred media mill. The initial pH of the sample is measured by digital pH meter (M/S. Toshcon Industries, Haridwar, India) and controlled at pH of 10.5 throughout the experiment. The concentrated NaOH and/or HCl solution was used in the experiment to control suspension pH to ensure minimal dilution of product slurry. Particularly we used 8 M NaOH and/or 8 M HCl solution for the said purpose. The samples are taken out from the mill chamber to measure the product size distribution at regular time interval of 0.5 h. A 2–3 mL of sample volume collected is diluted with 15–20 mL distilled water and pH was adjusted to 10.5 in all the cases. The samples were then sonicated for 3 min using ultrasonic probe (Ultrasonic, Germany) prior to size analysis.

2.3. Characterization

Zetasizer Nano ZS90 (Malvern Ltd., UK) instrument was used to measure the particle size distribution of the milled samples. It is working based on dynamic light scattering technique. The zeta potentials of the milled samples were measured based on laser doppler velocimetry (LDV) in the same instrument using Universal Dip Cell (Malvern Ltd., UK). All the particle size distributions measurement results presented are based on volume distributions of particle size. Volume mean particle size is used to denote the progress of grinding process. The samples were prepared by equilibrating respective nanosuspensions at pH 10.5 for 2 h for further powder characterization by BET, XRD, FTIR and TGA. The samples were dried overnight at 100 °C for 12 h in an oven. Then the dried powder samples were ground by mortar and pestle for better handling during analysis.

Specific surface areas of the samples were obtained by Gemini 2375 BET analyzer (Micromeritics, USA) using a sample dried overnight at a 300 °C in N_2 atmosphere. A mean particle size based on the specific surface area was calculated from the following equation:

$$D_{3,2} = \frac{6}{\rho S_w} \tag{1}$$

where $D_{3,2}$ is the surface volume mean diameter, ρ is the density of the material and S_w is the specific surface area of the sample determined by the BET test. TEM images were obtained with a Tecnai-20 (Philips, Netherlands), which at 200 kV provides 0.27 nm point resolution. The number mean particle size ($D_{2,0}$) from TEM was calculated by Eq. (2) using ImageJ software [19].

$$D_{2,0} = \frac{\sqrt{\sum_{i=1}^{n} d_i^2}}{n} \tag{2}$$