Synthesis of BaSO$_4$ Nanoparticles by Precipitation Method Using Polycarboxylate as a Modifier

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Abstract: Problem statement: Barium Sulfate (BaSO$_4$) is suitable for many applications because of its whiteness, inertness and high specific gravity. Approach: Nanoparticles of barium sulphate (BaSO$_4$) have been synthesized from barium nitrate by precipitation method in the presence of water soluble organic polycarboxylic polymer as a modifying agent. Transmission electron microscopy, Scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray powder diffractometry were used to characterize the products as well as laser grainmeter. Results: The results indicate that spherical BaSO$_4$ nanoparticles are obtained with poor crystalline and diameters ranging from 30-35 nm. Conclusion: The organic polycarboxylate shows as good modifier agent. So, this method can be employed to synthesize higher yield of BaSO$_4$ nanoparticles.

Key words: Barium sulphate, precipitation method, barium nitrate, water soluble organic, direct precipitation, crystal growth, micron scale, coupling agents, X-Ray Diffraction (XRD)

INTRODUCTION

Syntheses of inorganic powders with ultrafine size, controlled surface properties and controlled morphology attract increasing interest because of its important use in various fields. Barium Sulfate (BaSO$_4$) is suitable for many diverse applications because of its whiteness, inertness and high specific gravity (Bala et al., 2006). Barium sulfate is a kind of important inorganic chemical product as packing and additive in painting, coating, plastics and medicines fibers (Shen et al., 2007; Wu et al., 2007; Kucher et al., 2008). Nanometer barium sulfate has more scientific advantages of size reduction. Crystallization and precipitation processes are widely used in the chemical industry. One of the most well-known crystallization processes is the reaction of barium (Ba$^{2+}$) and sulphate (SO$_{4}^{-}$) ions into barium sulphate (BaSO$_4$), as shown in Eq. 1 (Oncul et al., 2006; Kieffer et al., 2009):

$$\text{Ba}^{2+}(\text{aq}) + \text{SO}_{4}^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(s) \downarrow$$

Liquid/liquid reaction is the main method of the preparation of nano-BaSO$_4$. This method has some divisions such as direct precipitation, micro emulsion (Adityawarman, 2005) membrane separation (Wu et al., 2007), microchannels reactor (Wang et al., 2009). Preparation of BaSO$_4$ particles has been widely studied in order to assess the effect of mixing, precipitation models, agitator speed and feed position on particle size distribution, crystal growth and morphology (Judat and Kind, 2004; Bala et al., 2005).

Many different approaches have been reported for preparation of BaSO$_4$ nanoparticles including the addition of different additives (Jones et al., 2003; Wang et al., 2005) induction by Monolayer and microemulsion (Nagaraja et al., 2007) The addition of additives and induction by LB monolayer could cause a significant change in morphology, but the size was generally in the micron scale rather than nanometer scale. The size and corresponding morphology obtained in W/O microemulsions (Chen et al., 2005) or reverse micelle approach could be controlled well by adjusting the molar ratio of water to surfactant. However, the product yield was rather low because of the poor solubility of salts in conventional microemulsions. There were also some reports about preparation of organo-modified BaSO$_4$, but the BaSO$_4$ obtained was in micron scale. Although preparation of organocapped BaSO$_4$ was earlier described, (Sui et al., 2004) the condition was not suited to the industry. Preparation of barium sulphate nanoparticles by use of tetradecanoic
acid, hexadecanoic acid and stearic acid as modifier was studied (Shen et al., 2007).

When inorganic fillers with surface functional groups reach the polymer matrix, it can be expected to enhance stiffness and impact properties simultaneously (Li et al., 2002; Bala et al., 2006). However, the surface of inorganic particles (e.g., BaSO₄) is hydrophilic, so it is not easy to disperse these particles in a lipophilic matrix. For this reason, it is very important to conduct surface modification of BaSO₄. One of the several ways to achieve a good dispersivity is to modify the hydrophilic particle surface so that it is lipophilic in nature. For this purpose various coupling agents, which are capable of introducing a certain functional group onto the particle surface, have been employed: Titanate coupling agents (He et al., 2005), silane coupling agents (Bala et al., 2006) and organophosphonic acids (D’Andrea and Fadeev, 2003; Sheng et al., 2004). This study aims to synthesize nanoparticles of barium sulphate (BaSO₄) from barium nitrate by precipitation method in the presence of water soluble organic polycarboxylic polymer as a modifying agent.

MATERIALS AND METHODS

Chemicals and instruments: The starting materials used in this study were Barium nitrate, ammonium sulphate and polycarboxylates. They were used without further purification. Double distilled water was used in all experiments. The prepared barium sulfate was characterized by using (SEM :JEOL JSM 6360 DLA, Japan), Transmission Electron Microscope ((TEM; Hitachi, H-800), Fourier transform Infrared (FT-IR) spectra were measured using a Perkin Elmer 880 FT IR spectrometer by incorporating samples in KBr (1: 99 mg) disks to confirm the characteristic vibrational bands, with resolution of 4 cm⁻¹, X-ray Diffraction (XRD) pattern of BaSO₄ was recorded on (M/S. Shimadzu Instruments, Japan) diffractometer XRD 7000 with Ni filtered Cu Kα as a radiation source at 2θ scan speed of 4° min⁻¹ and the particle size distribution was analyzed by L4 submicron particle size analyzer He-Ne Laser beam, Fluoride, USA.

Preparation of the samples:

**Direct Precipitation (DP) procedure:** 50 mL 0.1 M Ba(NO₃)₂ was added to 50 mL 0.1M (MH₄)₂SO₄ in the presence of water soluble organic polymers as modifier agent. The solution was added dropwise into the flask while stirring at room temperature with dispersant at strong mechanical stirring 2000-2500 rpm.

The steady drop rate was 20 drops min⁻¹. Gelatinous white precipitates were formed instantly. The precipitates were separated from the mother liquid by centrifuged at 3000 rpm for 20 min. and then the supernatant solution was discharged and the solid was redispersed in deionized water. This process was repeated three times in order to rinse the particles. After the last centrifugation, sedimented particles were dried in the microwave oven. The products were slightly grinded for analysis (Bala et al., 2005; Gupta et al., 2010).

Figure 1 shows the IR spectra of polycarboxylates 1 and 2. Note the band around 3400 cm⁻¹ for H₂O. The band at near 3000 cm⁻¹ for carboxylic acid O-H stretch also for, in the same region, the C–H stretching bands of both alkyl and aromatic groups. The carbonyl stretch C = O of a carboxylic acid appears as an intense band from 1760-1690 cm⁻¹. The C = C stretch band is at 1640 cm⁻¹. The C-O stretch appears in the region 1320-1210 cm⁻¹ and the O–H bend is in the region 950-910 cm⁻¹ and 1440-1395 cm⁻¹ from C-H bending bands in the same region (Khenifi et al., 2007).

RESULTS AND DISCUSSION

**TEM micrographs:** The TEM micrograph (Fig. 2) shows that the BaSO₄ particles are nearly elliptical and have a round shape. The particle size is between 6 and 26 nm, with an average size of 18 nm. In addition, there are some uniform mesopores in the particles and the diameter of the cavities is about 6-8 nm. These regions appear brighter because they have absorbed fewer electrons than their surroundings. The larger particles contain more pores and the
number of pores decreases as the diameter of the particles decreases, especially in small particles that only contain one pore. The high dispersibility of the powder in water might be related to the mesopores of the particles. The formation of the mesoporous structure is related both to nucleation and to the growth mechanism of the BaSO$_4$ particles. Judat and Kind (2004) and Nagaraja et al. (2007) investigated the particle morphology and internal structure (the cavities contained within the particles) of precipitated BaSO$_4$. They showed that BaSO$_4$ grows according to a combined mechanism involving molecular and aggregative growth. The pore size increases with increasing supersaturation.

**SEM Micrographs:** The SEM images (Fig. 3-c) shows that the spherical shell type nanoparticles are distributed uniformly. The larger particles contain more pores and the number of pores decreases as the diameter of the particles decreases, especially in small particles that only contain one pore. This reveals that the high dispersibility of the powder in polycarboxylate might be related to the mesopores of the particles and the high rate of adsorption of polycarboxylate onto their surfaces. The formation of the mesoporous structure is related both to nucleation and to the growth mechanism of the BaSO$_4$ particles (Nagaraja et al., 2007).

**XRD spectra:** Figure 4 shows the XRD pattern of nano barium sulfate. It is shown that the nano barium sulfate composed mainly from barite. All of the peaks could be indexed as a typical orthorhombic structure of BaSO$_4$, with crystalline cell constants $a = 7.144$ Å, $b = 8.865$ Å, $c = 5.445$ Å, which were basically in agreement with the reported values (JCPDS No. 80-0512) (Salah et al., 2009; Shen et al., 2007). The crystallite sizes of the sample are estimated from the line width of the (212) XRD peaks.
Fig. 4: XRD patterns of Nano BaSO₄

Fig. 5: FT-IR spectra of Nano BaSO₄

Fig. 6: Size distribution of BaSO₄ particles prepared
When polycarboxylate polymer was first added into water the PRCOO\(^{-}\) was fully released. Ba\(^{2+}\) was relatively surplus because SO\(^{4-}\) was dropped into Ba\(^{2+}\) in the process. Polycarboxylate P(RCOO\(^{-}\)) acted as an inducer to attract Ba\(^{2+}\) via electrostatic forces. With the addition of SO\(^{4-}\), BaSO\(_4\) crystals formed gradually. PRCOO\(^{-}\) still covered the surface of the BaSO\(_4\) crystals, resulting in the inhibition of further growth of BaSO\(_4\) nanoparticles, which was the reason for smaller size and uniform distribution of particles. During the process, polycarboxylate two roles: inducer and inhibitor. The average diameter of BaSO\(_4\) nanoparticles decreased in the order of addition of tetradecanoic acid, hexadecanoic acid and stearic acid, which was possibly related to the chain length of organic acid. The longer the chain length, the greater the steric hindrance (Shen et al., 2007).

## CONCLUSION

We have synthesized BaSO\(_4\) nanoparticles using water soluble organic stabilizing agent, polycarboxylate. Nanoparticles crystallize in the orthorhombic structure. FT-IR and electron microscopy studies confirm that the nanoparticles free from the surfactant and they are in the range of 30-55 nm. This method can be employed to synthesize higher yield of BaSO\(_4\) nanoparticles.

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