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Supercritical ethanol drying of zinc borates of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ and $ZnO{\cdot}B_2O_3{\cdot}2H_2O$

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ABSTRACT

Supercritical ethanol (SCE) drying of zinc borates was investigated to obtain dry zinc borate nanoparticles and to elucidate possible chemical interactions between zinc borates and ethanol. Commercial and synthesized $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ and $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ samples were dried by both conventional and SCE drying methods and the products were compared. Zinc borates were characterized using X-ray powder diffraction (XRD), thermo gravimetric analysis (TGA), Fourier transform infrared (FTIR) analysis, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and helium pycnometer. Zn and B contents of samples were also determined by analytical titration. It was found that zinc borate of $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ decomposed completely into zinc oxide and boric acid. However, zinc borate having oxide formula of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ decomposed partially to form anhydrous zinc borate, zinc oxide, water and boric acid during the SCE drying carried out at 250 °C and 6.5 MPa. Boric acid and water were extracted from both of zinc borates by supercritical ethanol. The extraction of boric acid by ethanol in the SCE drying of zinc borates is an important result which can be utilized in the production of boric acid from water insoluble natural minerals, e.g. colemanite. The boric acid–ethanol solution could be directly utilized in the synthesis of ethyl borate.

1. Introduction

Zinc borates are important engineering materials which have been widely used in various industries, such as flame retardant agent in polymers [1–3], preservative in wood products [4], corrosion inhibitor in coating and lubricating additive in industrial oils [5]. In most of those applications, particle size and morphology have become substantially important parameters as they determine function of material where they are used. There is a number of different zinc borate species defined in the literature, and each of them has specific application based on its unique properties. The feature of zinc borate is usually determined by several factors, such as B_2O_3/ZnO molar ratio, the amount of water and bonding type of water molecule to the main structure. In a general approach for the characterization of hydrated zinc borates is that when the number of water molecule in the structure is less, dehydration onset temperature rises significantly. For instance, $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ has a relatively high dehydration temperature of 415 °C thus; it is mainly preferred for polymers which require a high processing temperature [6]. However, the bonding type of water molecule in the structure of metal borate has also significant effect on the dehydration temperature. It was pointed out that the removal of crystalline water is more easily achieved than the removal of water which is in the form of hydroxyl groups in the structure.

The production of zinc borate ($2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$) from boric acid and zinc oxide was studied using different approaches [7–11] in the literature. Those studies were mainly interested in synthesis of micron sized product and optimization of reaction parameters. However, recent studies have focused on the production of nanosized zinc borate species, as particle size of product became important in many industrial applications. The major challenge in synthesis of inorganic nanoparticles is the accurate control of particle size and morphology which is directly related to processing methods. There are mainly two approaches known for the formation of nanomaterial: bottom-up and top-down methods. Bottom-up approach deals with controlling of the particle size in the reaction step and the prevention of nanoparticles' agglomeration. On the other hand, top-down approach deals with the size reduction of formed materials into nano scale by using conventional physical methods.

Hydrophobic zinc borate nano flakes were synthesized by employing solid–liquid reaction of zinc oxide and boric acid in the presence of oleic acid [12]. A nano zinc borate with amorphous phase was obtained in the presence of ammonia solution from borax and zinc nitrate as raw materials [13]. In most of

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the conventional approaches to produce nanostructured materials include thermal treatment, such as sol–gel [14], precipitation [15], and hydrothermal [16] techniques. During thermal drying, particle agglomeration problem occurs due to the influence of interfacial tension [17]. Supercritical fluids have been used in synthesis and processing of nanoparticles as they have tunable properties which enable the control of parameters in reaction media. When nanomaterials or nanostructures are synthesized, a supercritical fluid drying is usually used to control particle agglomeration or to preserve the structural configuration e.g., silica aerogel and electronic wafers. The supercritical fluid drying, where the solvent is removed at above its critical temperature (Tc) and pressure (Pc), is suggested to overcome the problem of nanoparticles clustering. In fact, in the supercritical region both liquid and gas viscosities become equal and there is no liquid–gas interface and no capillary pressure. A variety of supercritical fluids such as carbon dioxide, ethanol, and methanol have been used for drying different materials. For instance, supercritical ethanol drying was used in the synthesis of hexagon γ-alumina nanosheets [18] and silica aerogel was produced by supercritical carbon dioxide drying [19]. Some metal oxide nanoparticles were formed using supercritical synthesis technique in subcritical and supercritical conditions [20–22]. Taking into account the physical and chemical properties of material that will be dried, supercritical fluid drying technique might be used more effectively.

In the production of nano sized zinc borate, the first time oleic acid was used as a modifying agent in the reaction between borax decahydrate and zinc sulfate heptahydrate [23,24]. Although the nano discs of zinc borate with particle diameter of 100–500 nm were produced in the reaction, they agglomerated during thermal drying as pointed in their SEM microphotographs. The problems encountered in the preparation of zinc borate using supercritical carbon dioxide drying was pointed out in our previous study [25]. Supercritical ethanol drying was applied to several borate compounds, such as zinc borates [5], magnesium borates [26] and titanium borates [27]. Before the present study, supercritical ethanol drying technique was used to obtain nano sized zinc borate which was formed from borax and zinc nitrate [5]. In that study, authors did not take into account the interaction of zinc borate and ethanol at the temperature in which synthesized zinc borate decomposes. Thus, the interaction between zinc borates and ethanol was aimed to be investigated in this study.

Zinc borates formed by precipitation process from aqueous solutions are wet with water. This water can be replaced with ethanol by washing the precipitates several times with ethanol and the precipitate could be dried from ethanol under supercritical conditions. Since there is no interface between liquid and gas phases there is no interfacial tension between solid particles under supercritical conditions. This method was applied to obtain zinc borate nanoparticles by Dong and Hu [5]. Particles with higher surface area and better lubrication efficiency were obtained by supercritical ethanol drying compared to the particles obtained by conventional drying. The final product was shown to be crystalline by X-ray diffraction.

Ethanol rather than water was used as the supercritical drying solvent due to its lower supercritical temperature and pressure 513.9 K and 6.1 MPa than that of water, 647 K and 22.1 MPa. Since zinc borate was stable to heat in dry state at the supercritical temperature of ethanol, using ethanol as supercritical fluid was a good choice. Ethanol was also selected as a supercritical solvent for the removal of water wetting zinc borate particles since it has good solvation power for water. However the solid particles should be chemically stable in supercritical ethanol for nanoparticle production. The present study was made to elucidate the behavior of zinc borates under supercritical ethanol drying conditions. The interaction between zinc borate and ethanol may result in formation of different materials, such as zinc borates with lower hydration degree and B_2O_3 content, zinc oxide, and ethyl borate.

The aim of this study is to use SCE drying for obtaining dry zinc borate nanoparticles and to investigate the interactions between zinc borates and ethanol during SCE drying. For this purpose, commercial $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ and synthetic $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ produced from boric acid and zinc oxide, and $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ obtained from borax and zinc nitrate were dried by SCE drying and outputs of this process, powders and the ethanol phase, were characterized.

2. Experimental

2.1. Materials

Sodium borate decahydrate (borax) (99.5–105.0%) and zinc oxide (99.9%) from Sigma–Aldrich, boric acid (99.99%) from Aldrich, zinc nitrate hexahydrate (99.9%) from Fluka were used in the production of zinc borate species. Commercial zinc borate (Firebrake ZB) from US Borax firm was also processed in SCE drying experiments. D-Mannitol that used in titration was supplied from Sigma–Aldrich. De-ionized water and ethanol (99.8%) obtained from Riedel were used in washing and supercritical drying, respectively. 0.1 N NaOH and 0.1 M EDTA solutions were used in the determination of B_2O_3 and ZnO contents of zinc borate samples.

2.2. Production of zinc borate

Zinc borate species were produced by using two different raw material pairs. In the first, zinc borate was produced using 4.7 mol dm^{-3} boric acid and equivalent amount of zinc oxide regarding to the B_2O_3/ZnO molar ratio of 2 at 90 °C for 5 h. In the latter, zinc borate was produced by using 50 ml 1 mol dm^{-3} borax decahydrate and 50 ml 1 mol dm^{-3} zinc nitrate hexahydrate at 70 °C for 5 h reaction time. Both reactions were carried out at 900 rpm mixing rate in 0.30 dm^3 stainless steel reactor having external heating element with a four bladed mechanical stirrer. Temperature of reactants was maintained using a heating tape that was controlled by a temperature controller.

The prepared precipitates were washed using de-ionized water to remove the unreacted boric acid in the first method and unreacted zinc nitrate and sodium borate decahydrate and by product sodium nitrate in the second method. Different portions of the samples were either conventionally dried in air circulating oven at 110 °C or by SCE drying.

The dried zinc borate powders were tested for sublimation of boric acid at the ethanol critical temperature, 250 °C by using a glass sublimation tester. Samples under vacuum were heated at 250 °C for 30 min and any water formed was removed by vacuum, any condensable solid was condensed at the upper surface of sublimator.

2.3. Supercritical ethanol (SCE) drying of zinc borate

The supercritical ethanol drying system that was used in the experiments is shown in Fig. 1. Zinc borate samples that were produced in our laboratory were firstly washed by water and then washed by ethanol to remove water before SCE drying. After washing, approximately 8.0 g of zinc borate sample was placed into a high pressure reactor having 0.3 dm^3 volume.

Commercial zinc borate samples were also used in SCE drying as obtained. The amount of ethanol required to get supercritical conditions in the reactor was calculated as 0.11 dm^3 considering ethanol specific volume at supercritical conditions and reactor volume. Before heating the system, nitrogen gas was passed through the system to remove remaining oxygen in the reactor and pipelines. The