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Mechanochemical synthesis and investigations of calcium titanate powders and their acrylic dispersions

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Abstract

In this paper we studied calcium titanate ($CaTiO_3$) nanopowders obtained via a mechanochemical method assisted by microwave irradiation from calcium oxide and titanium dioxide, as well as its suspensions with addition of acrylic-poly(ethylene glycol) suspensions (SAP) obtained using microwave irradiation as a stabilizing agent. Experiments carried out using X-ray diffraction technique confirmed success of mechanochemical synthesis assisted by microwave irradiation and scanning electron microscopy images allowed to determine the structure as well as dimensions of $CaTiO_3$ nanopowders. Suspensions of $CaTiO_3$ and SAP were examined and the results showed relationships between the SAP concentration and both viscosity and stability. Both viscosity and stability are significantly increased upon addition of SAP and the dependency is nearly linear for higher SAP concentrations. Based on the results, we conclude that addition of SAP allows to successfully stabilize $CaTiO_3$ nanopowders and the stabilizing effect can be explained by both electrostatic and steric forces.

Keywords: Calcium titanate; Perovskite-type; Mechanochemical synthesis; Polymeric dispersant; Sedimentation rate

1. Introduction

The last two decades saw an intensive research in the field of ceramic materials with a perovskite-type structure due to their great potential to cover a wide range of applications. Among these perovskites, titanates appear to be the most appealing because of their versatile properties. A good example of these materials is calcium titanate ($CaTiO_3$), which exhibits properties dependent on its chemical makeup and number of defects in its crystal structure and thus has a vast range of potential technological applications. One of its most appealing features is the possibility to alter the ionic or electrical conductivity by inducing phase changes in the lattice. This alone allows $CaTiO_3$ to be used in various electrochemical applications, such as piezoelectric.[1–5] Furthermore, titanates can be used in both heterogeneous and photo-catalysis,[6–9] as well as in manufacture of radioactive wastes storage containers.[10,11]

The challenge lies in developing a synthesis method which would lead to titanates of uniform structure. These materials are often synthesized in a high-temperature processes,[12,13] which result in neither homogenous nor fine-crystalline materials, which negatively impacts their electrical properties. Other commonly used techniques for obtaining finely crystalline calcium titanate include sol–gel processing,[14,15] co-precipitation[16] and hydrothermal methods.[17] Most of these methods allow producing materials with excellent properties; however they are complicated and require use of organic solvents or precursors. Over the last few years, new methods have been developed in order to overcome the drawbacks and difficulties of those mentioned above. For example, a polymer precursor method was developed and then as synthesized materials were treated using adapted microwave oven.[18,19] A very interesting approach to synthesis of $CaTiO_3$ with microtubular structure and rectangular cross-section was recently reported by Li et al.[20] Such a morphology of $CaTiO_3$ is highly difficult to be achieved basing on bulk starting materials, therefore Li et al. successfully used titanate nanofibers. Also Yang et al.[21] have recently published results of their work, reporting successful synthesis of hollow

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crystals of $CaTiO_3$ along with explanation of the mechanism of their formation.

An alternative method, and one that fulfills the requirements of *green chemistry*, is mechanochemical.[22–25] This promising and developing technique, relying on.[26–31]

Colloidal suspensions are defined as dispersions of polymer molecular particles of sizes ranging from 1 nm to 1 μm or where discontinuities of phases occur at such distances.[32] Due to their properties, colloidal suspensions are widely used and investigations of their properties are of great interest. A property which is crucial when evaluating suspensions is their stability over time. There are a number of interactions between particles in suspension, but two of them are especially important as they ensure stability of polymeric dispersions of ceramics: charge/electrostatic and steric forces. The first type of interactions provides stabilization because colloidal particles may carry electrostatic charge which prevents aggregation, as identical charges mutually repel. Such a type of stabilization is observed in colloidal suspensions where ionic polymers are present. Their stabilizing efficiency is well known and confirmed. However, it may be diminished by presence of surface or other ionic solution impurities, addition of salts as well as other additives with different surface charge properties.[33,34] Since this kind of stabilization is charge-dependent, it may be investigated via pH measurements, and we opted for this method. The pH affects the net particle surface charges, as well as the dissociation degrees of carboxylic groups and the conformation of the polymer chain, leading to variation in the adsorption behaviors of the polymer on particles. The second type of stabilization, called steric stabilization, is generally considered to arise from two factors: a volume restriction component and a mixing or osmotic component, involving compression of the adsorbed layer causing an increase in polymer concentration. It is also important to assess the interparticle forces that may be present in concentrated suspensions and this is typically done by rheological investigations, such as yield stress measurements. Knowledge of the effect of polymer adsorption on the electrochemical and rheological properties of mineral suspensions is of a great industrial importance.[35–37]

Therefore, in this paper, we report the obtention of pure $CaTiO_3$ nanopowders by means of mechanochemical synthesis assisted by microwave irradiation and their morphological characteristics.

2. Experimental details

2.1. Synthesis materials and procedures

All materials used were oxides: CaO (Sigma–Aldrich, 90% $M = 153.33$ g/mol), TiO_2 (Evonik Degussa P25 GmbH, 98.0%, $M = 79.90$ g/mol).

A stoichiometric ratio of the oxides to $CaTiO_3$ was mixed by hand in an agate mortar in order to obtain a homogenous mixture which then was subjected to mechanochemical treatment in a high-energy planetary ball-mill, Activator 2S (Novosibirsk Corp., Russia). Milling was conducted at room temperature in air. A 250 mL reaction vessel was used, along with Cr–Ni steel ball-bearings of 10 mm in diameter. The vessel was rotated at 1100 rpm for 1.5 h, with a ball-to-powder weight ratio (BPR) of 40:1.

Table 1
Compositions of $CaTiO_3$ suspensions stabilized by SAP.

$CaTiO_3$ (g)	Water (ml)	SAP (g)	SAP (wt.%)
1.00	100	0	0
1.00	100	1.00	50
1.00	100	2.00	67
1.00	100	3.00	75
1.00	100	4.00	80
1.00	100	5.00	83

As a suspension-stabilizing agent we used acrylic-poly(ethylene glycol) suspensions, which we called SAP and synthesized using microwave irradiation. Appropriate amount of acrylic acid was mixed with potassium hydroxide (KOH) and poly(ethylene glycol). Ammonium persulfate ($(NH_4)_2S_2O_8$) and N,N′-methylenebisacrylamide were both added as an initiator and a cross-linking agent, respectively. A dispersion containing 250 ppm of silver and stabilized by poly(ethylene glycol) was also added. The reaction mixture was then placed in a microwave reactor (600 W, manufactured by Milestone Srl.), where it was treated for 3 min without stirring. The temperature of the reacting mixture was observed continuously throughout the process and kept at 90–95 °C. The resulting product (SAP) was solid and it formed very viscous but uniform jelly-like suspensions.

Dispersions of $CaTiO_3$ were prepared using acrylic-poli(ethylene glycol) suspensions (SAP) as a dispersant polymer matrix, synthesized as above (see also:[38–40]). Compositions of the suspensions are shown in Table 1. It can be seen that the experiments covered suspensions with various concentrations of SAP, while $CaTiO_3$ concentration was kept constant.

2.2. Characterization of as-synthesized materials

The as-synthesized materials were analyzed using powder X-ray diffraction (XRD) with a CuK_α source on an X'Pert Philips instrument, from $2\theta = 10°$–$90°$ with an increment of 0.01°. Identification of the material was accomplished by consulting a JCPDS table. The surface area of the materials was determined using BET physical absorption isotherms, using an Accelerated Surface Area and Porosimetry Analyzer (ASAP) 2020 from Micrometrics. Scanning Electron Microscopy images were obtained using JEOL JSM 7500F with BSE detector (Back Scattered Electrons). The stability of the dispersions was investigated via pH measurements performed over 10 days with constant $CaTiO_3$ and varied SAP amounts. The dynamic viscosities of the dispersions were measured at room temperature (20 °C) using an Anton Paar DV-2 P viscometer with mandrel R2. Particle stabilization in the suspensions was examined by performing sedimentation experiments. Each suspension was poured into sealable graduate test tubes and the initial suspension heights (h_0) were noted. After 1 and 24 h, the sediment heights