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Synthesis of ceria (CeO_2 and CeO_{2-x}) nanoparticles via decarbonation and Ce(III) oxydation of synthetic bastnäsite ($CeCO_3F$)

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HIGHLIGHTS

- An original method to synthesize ceria nanoparticles (CeO_2 and CeO_{2-x}) from bastnäsite.
- New experimental conditions to produce ceria with oxygen vacancies CeO_{2-x}.
- (TGA/DSC) coupled with (μGC/MS) performed to investigate on the ceria formation.
- Specific hydrothermal conditions to which bastnäsite can be formed.

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ABSTRACT

Ceria (CeO_2) crystalline compound is widely used as a catalyst or catalyst support and many other applications. However, the studies are continuing with a view to improving existing methods and/or developing innovative routes to obtain well-controlled shapes and sizes of ceria nanoparticles. In the present study, we report an original method to synthesize ceria nanoparticles (CeO_2 and CeO_{2-x}) by using two independent stages: (1) the precipitation of bastnäsite-rich material under hydrothermal conditions (90 and 300 °C) and (2) the calcination of powdered basnäsite-rich material at different temperatures (500, 1000 and 1600 °C) and under different atmospheres (air, Ar, N_2 and secondary vacuum). In addition, simultaneous thermal analyses (TGA/DSC) coupled with gas chromatography (μGC/MS) were performed in order to investigate on the ceria formation during bastnäsite de-carbonation and its thermal behavior at high temperature (until 1600 °C) under three different gas atmospheres (air, Ar and N_2). Herein, ceria was in-situ formed independently on the gas investigated atmosphere. This means that sufficient oxygen was also available in the so-called inert atmospheres (Ar and N_2) to oxidize the Ce(III) contained in Ce-carbonates to Ce(IV) constituting ceria cubic structure. Moreover, μGC/MS measurements confirm that in-situ formed ceria CeO_2 at about 600 °C is then partially reduced to CeO_{2-x} at high temperature after 1000 °C because an increase in oxygen was clearly detected in expelled gas during heating process. This fundamental experimental study provides the hydrothermal conditions to which Ce fluorocarbonates could be formed in natural environments. In addition, new experimental conditions to produce ceria with oxygen vacancies CeO_{2-x} without reducing gas agent and at lower temperature are also provided in this study.

1. Introduction

Cerium being the most abundant metal among the rare earths, it is found in a number of minerals such as bastnäsite, monazite, gadolinite, fergusonite, samarskite, xenotime, yttrocerite, cerite,

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allanite (or orthite), etc. Among these, bastnäsite fluorocarbonate ((Ce, La, Y)CO_3F) is the most important source of cerium and probably the most abundant in the nature [1–3]. Fluorocarbonates can have industrial applications related to their optical and magnetic properties, but, these rare minerals are systematically associated to other minerals and they systematically contain other structural rare or major elements that may restrict their utilization [3,4]. In this way, the synthesis of high-purity flurorocarbonates with controlled rare element composition, particle size and crystal morphology represent a significant challenge in materials science. Moreover, their precipitation under hydrothermal conditions could provide insights into the mobility of rare-earth elements during fluid–rock interactions in natural systems [5]. In this context, we report here specific hydrothermal conditions to which cerium fluorocarbonates such as bastnäsite ($CeCO_3F$) and Lukechangite ($Na_3Ce_2(CO_3)_4F$) could be formed in natural environments. We note that significant light rare earth elements (REE) reserves occur as fluorocarbonate minerals, mainly bastnäsite. However, despite the importance of these minerals, very little is known about the physicochemical conditions controlling their formation and experimental studies relevant to REE fluorocarbonate mineral stabilities are rare [6,7].

On the other hand, the cerium processed from bastnäsite and other natural cerium sources is typically used as ceria (CeO_2) nanoparticles or a wide variety of ceria-based nanomaterials (e.g. [8,9]). Ceria or cerium oxide exist also as natural mineral (called as cerianite) that has been identified as a secondary mineral at the many localities worldwide, including, weathered phonolites and nepheline syenites, hydrothermal veins, granite pegmatite, alluvial deposits, alkaline pegmatite, etc. [10], but, this accessory or minor mineral in host rocks is not directly exploited and used at our knowledge. Conversely, synthetic cerium oxide (CeO_2) having cubic structure is the most important oxide related to its extraordinary chemical properties (acid–base and oxidation-reduction behavior), thermal stability (melting point $= 2400$ °C) and oxygen mobility [9,11–13]. It has found its applications in catalysis, luminescent materials, fuel cell, free radical scavenger, gas sensor, cosmetic material, optical additives, polishing materials, water splitting, ceramic pigments, etc. [9,12,14–16]. However, the most important applications of ceria nanoparticles are as catalyst, catalyst promoters or catalyst supports. For example, control of toxic combustion gas emissions (e.g. in automobile mufflers) via oxidation of CO and reduction of NO_x [9 and references therein]. This is due to high oxygen mobility allowing reversible reduction-oxidation cyclic reactions without disruption of the cubic lattice-structure [17]. Due to numerous applications of ceria, several methods of synthesis have been proposed in the last two decades such as sol–gel process, aqueous precipitation, electrochemical synthesis, hydrothermal and solvothermal synthesis routes, reverse micellar synthesis, microemulsion method, flame spray pyrolysis, sonochemical method, microwave-assisted method, etc. (e.g. [9,11,12,18]). Several of above methods require a second independent step by thermal treatment or so-called calcination ($T \geq 500$ °C) in order to obtain high-purity CeO_2 material. Studies are continuing with a view to improving existing methods and/or developing innovative routes to obtain well-controlled shapes and sizes of ceria nanoparticles.

The purpose of the present study was two-fold. Firstly, synthesize high-purity bastnäsite ($CeCO_3F$) using hydrothermal conditions. As above mentioned, bastnäsite is the most important source of cerium, but, very little is known about the physicochemical conditions controlling its formation in natural settings [6,7]. Herein, we provide specific hydrothermal conditions to which bastnäsite can be formed, but, it has coexisted with Petersenite $Na_4Ce_2(CO_3)_5$ and/or Lukechangite $Na_3Ce_2(CO_3)_4F$ depending on the temperature, both in minor proportion. Secondly, synthesize ceria CeO_2 nanoparticles by direct calcination of synthetic bastnäsite. For this purpose, recovered powdered Ce-carbonate material was calcined under air or secondary vacuum ($\approx 5 \times 10^{-6}$ mbar) at 500 or 1000 °C in a quartz tubular reactor. As expected, high-purity ceria CeO_2 nanoparticles ($S_{BET} = 30$ m^2/g) were obtained in air atmosphere, while CeO_{2-x} partially reduced ceria nanoparticles ($S_{BET} = 10$ m^2/g) were obtained under secondary vacuum. In complement to this basic investigation, simultaneous thermal analysis (TGA/DSC) coupled with gas chromatography (μGC/MS) were performed in order to investigate on the ceria formation during bastnäsite de-carbonation under non-isothermal conditions and its thermal behavior at high temperature (until 1600 °C) under three different gas atmospheres (air, Ar and N_2).

2. Materials and methods

2.1. Precipitation of bastnäsite fluorocarbonate $CeCO_3F$

250 ml of high-purity water with electrical resistivity of 18.2 MΩ cm, 10 g of NaOH, 12.5 g of $CeCl_3.7H_2O$ and 2.1 g of NaF were placed in a reactor (hastelloy C22 autoclave with internal volume of 0.6 L). This reactive suspension was immediately stirred during the reaction by means of a constant mechanical stirring system (400 rpm). The temperature of the suspension increased instantaneously to 26 °C due to the exothermic dissolution of NaOH in the system. At this reference temperature, CO_2 was immediately injected in the system at a pressure of 40 bar. The carbonation reaction started instantaneously as attested by the continuous consumption of CO_2, monitored by a pressure drop in the system, and an increase in temperature during the exothermic carbonation reaction. After about 5 h of carbonation reaction, a heat-aging step was performed from room temperature to 300 °C for a further 24 h. Herein, the total pressure was stabilized to 93 bar at 300 °C. The same synthesis procedure was also performed at 90 °C.

At the end of the experiment, the autoclave was removed from the heating system and cooled using continuous flow air. The residual CO_2 was degassed from the reactor after air-cooling period, i.e. when $T \leq 60$ °C. After water cooling at 60 °C the autoclave was disassembled, and the solid product was carefully recovered and separated by centrifugation (30 min at 12,000 rpm), decanting the supernatant solutions. The solid product was washed twice by redispersion/centrifugation processes in order to remove the soluble sodium carbonates formed during the synthesis. Finally, the solid product was dried directly in the centrifugation flasks at 80 °C for 48 h. The dry solid product was manually recovered and stored in plastic flasks for subsequent characterization (FESEM, XRD, TGA/DSC and N_2 sorption isotherms).

2.2. Synthesis of ceria CeO_2 nanoparticles by calcination

1 or 2 g of dry synthetic bastnäsite ($CeCO_3F$)-rich material (purity ≈ 70%) mixed with two other Ce carbonates (Petersenite (20%): $Na_4Ce_2(CO_3)_5$ and Lukechangite (10%): $Na_3Ce_2(CO_3)_4F$) obtained from above hydrothermal method (sub-Section 2.1) were thermally treated under air atmosphere or secondary vacuum ($\approx 5 \times 10^{-6}$ mbar) by using a quartz tubular reactor. Herein, two temperatures (500 and 1000 °C) were typically investigated. The same heating rate (30 °C/min) was used in all experiments. The duration of thermal treatment was arbitrary defined at five hours, but, for some experiments performed at 500 °C, the duration was prolonged to 4 days in order to investigate on the kinetics effect. At the end of experiment, the samples were cooled under their original atmosphere, i.e. in contact with atmospheric air or under vacuum. The dry solid product was manually recovered and stored