Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 1994–2005

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis and characterization of iron oxide particles using spray pyrolysis technique

Beril K. Ozcelik[a], Celaletdin Ergun[a,b,*]

[a]Istanbul Technical University, Mechanical Engineering Department, Beyoglu, Istanbul, Turkey
[b]Istanbul Technical University, Prof. Dr. Adnan Tekin, Materials Science & Production Technologies, Applied Research Center, Maslak, Istanbul, Turkey

Received 12 July 2014; received in revised form 17 August 2014; accepted 18 September 2014
Available online 13 October 2014

Abstract

Spherical nano-sized iron oxide particles were synthesized by a spray pyrolysis method using the aerosol technique described herein. The effects of reaction temperatures of 500, 700, 900 and 1100 °C; the type of carrier gas, i.e., air or argon; and the collection location of the particles, such as the flask collector or the tube exit, on the morphology and crystal structure of the iron oxide particles were investigated. It was observed that the crystallinity of the particles was increased by increasing the reaction temperature from 500 °C to 1100 °C. Particles collected from both the tube exit and the flask collector had a pure α-Fe_2O_3 phase when air was used as the carrier gas. These nanoparticles had sizes between 70 nm and 675 nm with uniform morphologies. The average particle sizes changed depending on the reaction temperature and collection location. On the other hand, depending on the reaction temperature, the particles collected from both the tube exit and the flask collector were Fe_3O_4 and/or α-Fe_2O_3 phase when argon was used as the carrier gas. Nanoparticles synthesized using argon as the carrier gas had sizes between 100 nm and 390 nm. A computational fluid dynamics (CFD) model of the horizontally positioned tube reactor was developed. Simulation results provided information about the residence time and the temperature distribution along the tube, which were observed to be correlated to the particle morphology.

Keywords: Spray pyrolysis; Nanoparticle; Iron oxide; CFD simulations

1. Introduction

Iron is the fourth most plentiful element and the most ubiquitous of the transition metals in the Earth's crust. However, advancements in the technological applications of iron have been delayed due to slow and insufficient research and limited mainly to structural applications. Recently, the magnetic and catalytic properties of nano-sized iron have opened up a new field of research [1]. In this context, one of the greatest challenges due most likely to the greatest weakness of iron is its reactivity, specifically with respect to water and oxygen. For this reason, iron may be coated with polymer or iron oxides, such as hematite (α-Fe_2O_3), magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) or wüstite (FeO). There are approximately 16 iron oxides that occur in the form of oxides, hydroxides or oxide–hydroxides [1,2].

Hematite is one of the important iron oxides that can exhibit unique combinations of features such as high corrosion resistance, non-toxicity, environmental compatibility, remarkable optical, electrical and magnetic properties as well as low cost [3–6]. α-Fe_2O_3 has been extensively used in different ways, such as in mixing agents for ceramics and rubber, pigments, gas sensors, and catalysts [7–9]. Recent studies have shown that α-Fe_2O_3 particles with different sizes and morphologies possess different chemical and physical properties. α-Fe_2O_3 nanostructures also find magnetic and biotechnological applications as well as applications in lithium ion batteries, drug delivery systems, etc. [10–12]. α-Fe_2O_3 nanostructures with different morphologies can

*Correspondence to: Istanbul Technical University, Department of Mechanical Engineering, Beyoglu 34437, Istanbul, Turkey. Tel.: +90 533 653 1988; fax: +90 212 245 0795.
E-mail address: ergunce@itu.edu.tr (C. Ergun).

http://dx.doi.org/10.1016/j.ceramint.2014.09.103
0272-8842/

be synthesized, such as nanowires [13], nanorods [14], nanotubes [15], ellipsoid-shaped particles [16], and hexagonal-pyramid-shaped particles [7].

Among the other iron oxides, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are the most interesting forms because of their strong magnetic signature. These oxides are by far the most commonly employed in biomedical applications due to their biocompatibility, superior chemical and thermal stability, hardness, high saturation magnetic moment (M_S=90 emu/g) [17] and non-toxicity [18].

Numerous methods for synthesizing and producing iron oxide particles have been developed over the past several years, such as (i) coprecipitation of iron salts, (ii) sol–gel processing, (ii) hydrothermal reactions, (iii) precursors hydrolysis, (iv) aerosol pyrolysis, (v) electrodeposition, (vi) flow injection, and (vii) reactions in constrained environments (liposomes, microemulsions) [19].

Quin et al. [20] obtained single-crystalline α-Fe_2O_3 nanocubes through a facile one-step hydrothermal synthetic route under mild conditions. The morphologies of the α-Fe_2O_3 samples, and the most probable formation mechanism, could be controlled by varying the reaction time, yielding nanocubes with side lengths of 100–200 nm. Hoa and co-workers [21] prepared Fe_3O_4 nanoparticles with an inner layer of sodium oleate and an outer layer of polyethylene glycol (PEG-6000) in air by the coprecipitation method; the average size of the Fe_3O_4 nanoparticles was approximately 25 nm. Huo et al. [22] synthesized an α-Fe_2O_3 hydrosol by the sol–gel method with $FeCl_3 \cdot 6H_2O$ as the raw material, and thin films of the material were prepared by the dip-coating technique. The particles were pseudocubic shaped, with a mean particle size of approximately 58 nm. Du et al. [23] selectively synthesized α-Fe_2O_3 and Fe_3O_4 nanowires with a diameter of approximately 100 nm and a length of tens of micrometers by a microemulsion-based method in combination with calcination under various atmospheres. The main technological differences among these various methods involve the types of precursors, the process temperatures, the unit operations, the scales at which the methods can be carried out, and most importantly, the particle size distribution and morphology of the final products.

Among the various particle synthesis methods that exist, spray pyrolysis is one of the most sophisticated process for synthesizing particles in a single step. Spray pyrolysis is a continuous flow process enabling low service costs compared to the costs incurred by other processes. In addition, this method can be easily implemented for the synthesis of other advanced ceramics with different chemical compositions because of its high chemical flexibility and the ease with which the process parameters can be controlled [24]. The generation of particles is based on a one-droplet-to-particle conversion mechanism. In this method, precursor solutions are first atomized into droplets, which are subsequently pyrolyzed (via evaporation, precipitation, drying, thermal decomposition and sintering) to become solid particles. The average diameter of the final solid particles can be roughly determined from the droplet size and solute concentration of the precursor solution [25–27]. Cabanas and co-workers [28] applied aerosol pyrolysis for the production of iron oxide particles using nitrate, citrate or organic water solutions and obtaining α- or γ-Fe_2O_3 and Fe_3O_4 particles. The average particle size was 0.3–2 μm in air when citrate was used as the precursor. Gurmen et al. [29] produced hollow, spherical α-Fe_2O_3 nanoshells via ultrasonic spray pyrolysis. The shell thickness of the hollow α-Fe_2O_3 spheres was approximately 30–100 nm depending on the reaction temperature.

In this research, α-Fe_2O_3 and Fe_3O_4 particles were synthesized by a spray pyrolysis technique using a laboratory-made spray pyrolysis unit. The structural and morphological changes in the particles due to the carrier gas and reaction temperature used were investigated. The experimental system was modeled by CFD to evaluate the effect of operation parameters on the characteristics of the produced particles.

2. Experimental procedures

2.1. Materials

All of the precursor chemicals were reagent-grade, and therefore, no further purification steps were performed. Iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) was dissolved in methanol at a

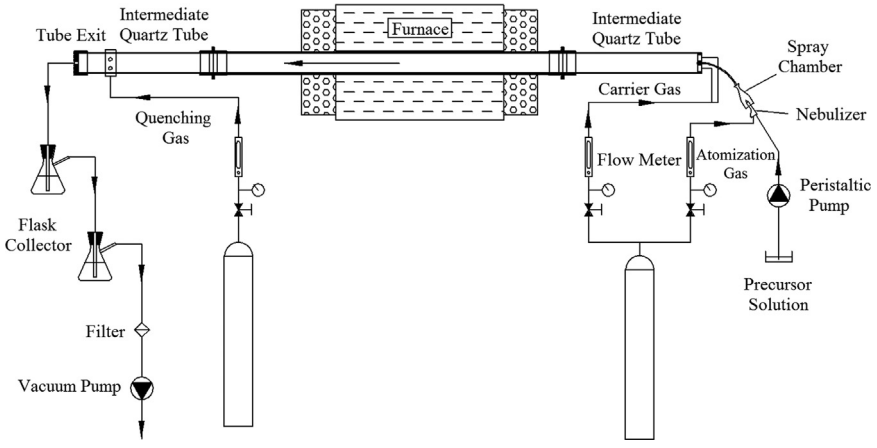

Fig. 1. Schematic diagram of the experimental apparatus.