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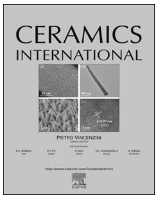

Effects of pH value on the microstructure and magnetic properties of solution combusted Fe_3O_4 powders

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ABSTRACT

Magnetite (Fe_3O_4) powders were prepared by solution combustion synthesis method using conventional and microwave ignition at various pH values of starting solution, adjusted by NH_4OH. The chelated species in dried gels were predicted by theoretical calculations and Fourier transform infrared spectroscopy. The combustion reaction rate strongly depended on pH values as investigated by thermal analysis. Phase evolution and structure characterized by X-ray diffraction method showed single phase and well-crystalline Fe_3O_4 powders which were achieved using conventional ignition at pH ≥ 7. However, the microwave ignition led to the formation of impure FeO phase together with Fe_3O_4. The microwave combusted powders exhibited the disintegrated structure in comparison with the bulky microstructure for conventionally combusted powders, as observed by scanning electron microscopy. Magnetic properties of the as-combusted powders studied by vibration sample magnetometry showed the highest saturation magnetization of 81.3 emu/g for conventional ignition at pH of 7, due to the high purity and large crystallite size.

1. Introduction

Solution combustion synthesis (SCS) as a complex self-sustained chemical process in a homogeneous solution of precursors is a versatile, simple and rapid process and suitable for direct synthesis of mass nanomaterials [1–3]. SCS employs an exothermic reaction between an oxidizer, typically metal salts, like nitrates, sulfates and carbonates and an organic fuel such as urea, glycine, citric acid, sucrose, etc. [4]. Several thermally coupled exothermic reactions along with dehydration and thermal decomposition of homogeneous solution take place by further heating, leading to the formation of at least one solid product and a large amount of gas [5,6]. Among various metal salts, the metal nitrates with the lower decomposition temperature, good solubility and the efficient oxidizing NO^{3-} group are generally used in solution combustion synthesis [7]. Moreover, the citric acid ($C_6H_8O_7$) as a weak organic tricarboxylic acid can be used as fuel, due to its high exothermicity and coordination ability toward cations [6]. The citric acid as a chelating agent can result in a more homogeneous mixing of cations and prevents from selective precipitation and/or phase separation which is beneficial for producing multicomponent oxides, e.g. spinels, garnets, perovskites, superconductors, etc. at low temperatures [8–10]. The formation of metal citrates strongly depends on the concentration of citric acid, pH and temperature [11]. Therefore, SCS parameters like fuel type, fuel to oxidant ratio and pH have to be carefully modified for efficient combustion as well as to produce well crystalline and high purity powders [3]. Furthermore, there are two different methods as conventional and microwave heating for igniting the precursor solution, affecting the physicochemical properties of the as-combusted powders, such as phase, morphology, particle size, surface area, etc. [12–14]. In the conventional heating, ignition began at a single point which was the most ready for this ignition and then progressed into the surrounding, because heat is transferred from the outside. However, the volumetric heating with the interaction of the electromagnetic field with electric and magnetic dipoles of the materials leads to multiple ignition points throughout the precursor, due to the generation of heat inside the material [15].

Magnetic spinel ferrite nanoparticles, e.g. magnetite (Fe_3O_4), are of great interest for magnetic fluids, biotechnology, biomedicine, magnetic resonance imaging, hyperthermia, data storage and environmental remediation, due to the excellent physical and chemical properties like high saturation magnetization (92 emu/g), chemical stability and low toxicity [16]. The electrical and magnetic properties of Fe_3O_4 powders can be tuned by oxidation state of iron, size and morphology of particles through synthesis method [17]. Among various synthesis methods such as high-energy ball milling, coprecipitation, hydrothermal and thermal decomposition [18–20], SCS has attracted considerable attentions due to its ability for production of Fe_3O_4 powders with high surface area and high saturation magnetization for electrochemi-

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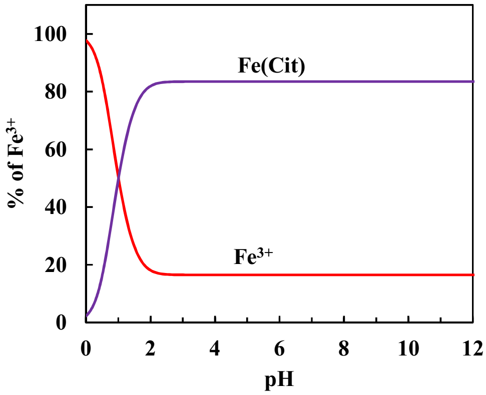

Fig. 1. The calculated concentration of ferric species in solution, as a function of pH at the fuel/oxidant molar ratio of 1 (Cit:$C_6H_5O_7^{3-}$).

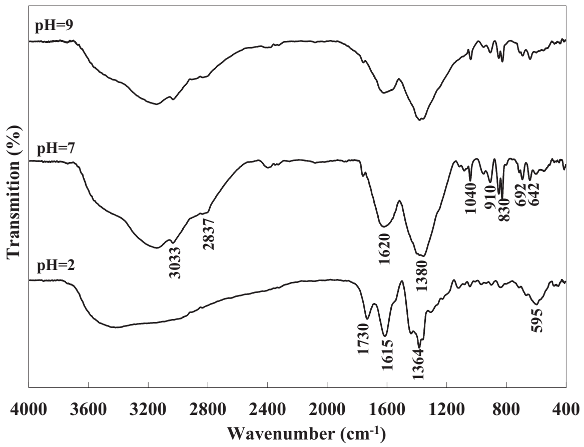

Fig. 2. FTIR spectra of the dried gels at 80 °C prepared at the various pH values.

cal and biomedical applications [21–24]. Zhang et al. [25] synthesized porous Fe_3O_4 powders by SCS using citric acid as fuel at various fuel to oxidant ratios (ϕ = 0.1–1.5). The highest saturation magnetization of 83 emu/g was achieved for the as-combusted Fe_3O_4 powders at ϕ = 0.36, due to its high purity and crystallinity. Manikandan et al. [12] showed the as-combusted Fe_3O_4 powders with the smaller crystallite size (20–25 nm), higher specific surface area (72.5 m^2/g) and higher saturation magnetization (66 emu/g) can be prepared by microwave ignition.

In the present work, the effects of solution acidity and microwave ignition on the combustion behavior, phase, microstructure and magnetic properties of the solution combusted Fe_3O_4 powders using the citric acid as fuel were reported. It was found out that the combustion reaction rate increased with the increase of pH, due to the formation of NH_4NO_3 in the dried gel. Furthermore, the microwave ignition led to the formation of FeO phase together with Fe_3O_4 for pH ≥ 7, while single phase Fe_3O_4 powders were formed in conventional ignition.

2. Experimental procedure

The required amounts of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) and citric acid ($C_6H_8O_7$) were dissolved in distilled water in which the fuel to oxidant molar ratio (ϕ) was considered as unity. After homogenization, the pH of solution was adjusted to 2, 7 and 10 with the addition of 25 wt.% ammonia (NH_4OH) solution under continuous stirring. The mixture was slowly evaporated at 80 °C until a viscous solution was formed. A part of the solution was poured into a round bottom flask and heated till to transform into a gel while by further heating up to a certain temperature, ignition reaction started from a point and

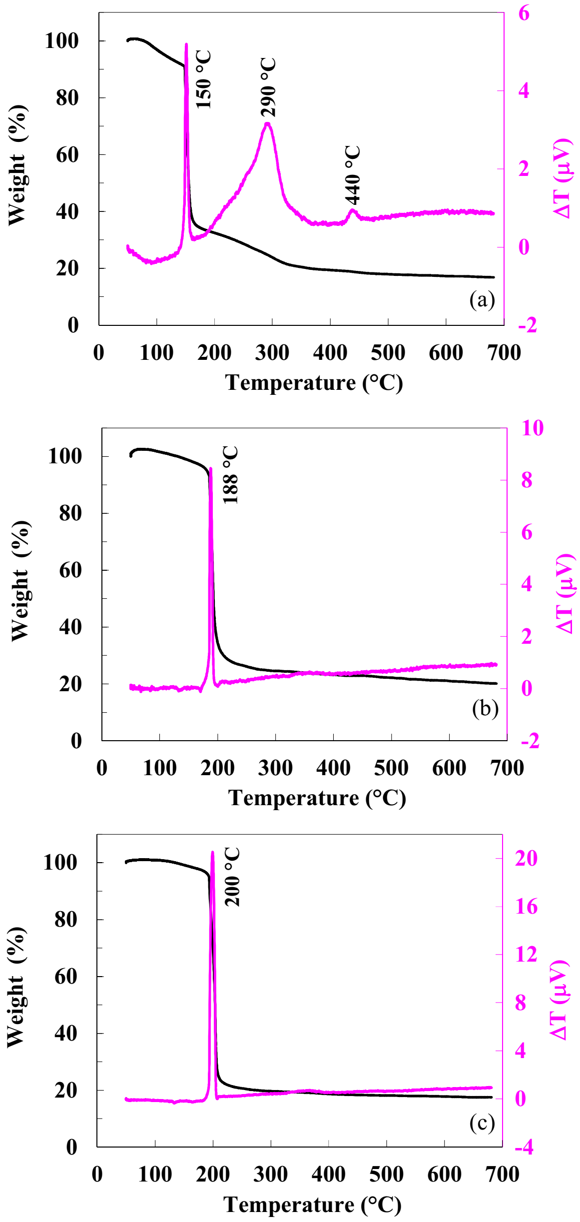

Fig. 3. TGA/DTA curves of the dried gel prepared at the different pH values of (a) 2, (b) 7 and (c) 9.

propagated spontaneously. Another part of the solution was poured into another round bottom flask and placed in a household microwave oven (2.45 GHz, 750 W) for 2 min. The combustion gases were bubbled in a large beaker filled with water. The obtained powders were hand-crushed with a pestle.

IR spectra in the range of 400–4000 cm^{-1} were measured by Fourier transform infrared (FTIR) spectrometer (8500S SHIMADZU). Thermal decomposition of the dried gels at 80 °C was examined by simultaneous differential thermal and thermogravity analysis (DTA/TGA) in air with the heating rate of 5 °C/min on the STA BäHR 503 instrument.

Phase evolution was analyzed by PANalytical X′pert diffractometer (XRD) using monochromatic CuKα radiation. The average crystallite size was calculated from the width (220) peak using Scherrer's equation. XRD patterns were also submitted to a quantitative analysis by the Rietveld method using MAUD software.

The morphology and microstructure of the powders were observed by TESCAN Vega II field emission scanning electron microscopy (FESEM).

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