

Influence of pH on the characteristics of cobalt ferrite powder prepared by a combination of sol-gel auto-combustion and ultrasonic irradiation techniques

S. S. Madani*, G. Mahmoudzadeh and S. Abedini Khorrami

Chemistry Department, North Tehran Branch, Azad University, Tehran, Iran

Cobalt ferrite (CoFe_2O_4) powders with nanocrystalline sizes were produced by a combination of sol-gel auto-combustion and ultrasonic irradiation methods employing a mixture of urea, thiourea and glycine as the fuel with the corresponding metal nitrates. The pH in the starting solution affects the combustion process, and then determines the particle size of the as-synthesized powder. The influence of the pH value on the gel auto-combustion and the phase composition of the synthesized powders have been studied with the help of scanning electron microscopy (SEM) observations, Fourier transform infra red (FTIR) spectroscopy and X-Ray diffraction (XRD) techniques. The synthesized powders had a particle size distribution in the range of 23-43 nm.

Key words: Cobalt ferrite, Nanocrystalline, Sol-gel auto-combustion, Ultrasonic irradiation, pH value.

Introduction

Magnetic nanoparticles offer great potential application in a variety of biomedical fields, such as improved contrast agents for magnetic resonance imaging (MRI) [1], cell separation [2], hyperthermia tumor treatment [3] and as magnetic field-guided carriers for localizing drugs or radioactive therapies [4]. A ferrite with a spinel structure which is formed by a nearly close packed fcc array of anions with holes partly filled by the cations can be represented by the formula AB_2O_4 , where A represents metallic ions located in A interstitial (tetrahedral) sites and B metallic ions located in B (octahedral) sites. Due to the large electronegativity of oxygen, the ionic type of bonds prevails in almost all oxide spinels [5]. The exchange interaction in spinel ferrites in which the antiparallel alignment of magnetic moments of the A-site with B-site is mediated by oxygen ions is called super-exchange interaction. The strength of the super-exchange interaction between the cations depends on the A-O-B bond angle, which is the largest for an angle of 180° [6].

It is worth mentioning that, most of the magnetic properties of CoFe_2O_4 strongly depend on the size and the shape of the nanoparticles, which are closely related to the preparation method. Various preparation techniques have been accordingly developed to produce CoFe_2O_4 nanoparticles including chemical co-precipitation [7], micro-emulsion [8], sol-gel method, sol-gel auto-combustion [9], hydrothermal [10], solvothermal [11], organic precursor method [12], ball milling [13], forced hydrolysis in a

polyol medium [14], mechanochemical method [15], sonochemical [16] and complexometric synthesis [17]. Among the many synthetic methods proposed, the sol-gel auto-combustion route, as a unique combination of the combustion and the chemical gelation process, is preferred in general because of its main advantages of inexpensive precursors, short preparation time, modest heating and relatively simple manipulations [39-41]. Although the sol-gel route yields more promising results in the synthesis of nanoferrites, several preparation conditions such as dilution, fuel/oxidant ratio, pH and temperature can have an impact on the formation of the ferrites and their properties [19].

Ultrasonic cavitation chemistry, an approach for synthesizing a variety of compounds with milder conditions is already the rage in materials technology. Over the last few years, this technique has also started to catch on in the materials science community as a way to speed discoveries in this area. The major advantage of this new method is that it affords a reliable and easy route for the control of both the synthetic process and nanostructure in advanced materials. Also, this process provides chemical homogeneity and reactivity through atomic level mixing within the precursor system, and phase-pure crystalline materials can be prepared by calcining at reduced temperatures [20].

In the present investigation, the influence of the pH value of a mixed solution on the combustion behavior of the precursor gel was studied.

Experimental

Materials and methods

Cobalt nitrate hexa hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck), iron nitrate nona hydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Merck), urea ($\text{CO}(\text{NH}_2)_2$, Merck), thiourea ($\text{CS}(\text{NH}_2)_2$, Merck), glycine

*Corresponding author:
Tel : +98-912-2709240
Fax: +98-21-22421047
E-mail: se_madani@yahoo.com

($C_2H_5NO_2$, Merck) and NH_4OH (Merck) were obtained of analytical grade. All materials were used without further purification. Deionized water was used for all the experiments.

$CoFe_2O_4$ powders were synthesized from sol-gel auto combustion by ultrasonic irradiation (HF-Frequenz 35 kHz, 240 W/ Made in Germany) methods. The phase identification of the burnt powder of $CoFe_2O_4$ was done using XRD (Model : XPERT- MPD, Philips with operated at 40 kV and 40 mA). The structural morphology was investigated using SEM (Phillips XL30 with 16 kV operating voltage). An infrared study of calcined powders was done using an FTIR instrument (NICOLET-NEXU-870).

General procedure

Cobalt ferrite nanocrystalline powders with a composition of $CoFe_2O_4$ were synthesized by a combination of sol-gel auto-catalytic combustion and ultrasonic irradiation techniques. A flow chart for preparing nanocrystallite ferrite is shown in Fig. 1. The detailed process can be described as follows. An appropriate amount of nitrates and fuel (a mixture of urea, thiourea and glycine with a molar ratio 1 : 1 : 1) were first dissolved into deionized water to form a mixed solution. The molar ratio of metal nitrates to fuel was 1 : 1.2. Ammonia was added to change the pH value of the mixed solution from 5 to 9. Then the mixed solution was poured into a dish and heated at 85 °C under constant stirring to transform into a dried gel in a N_2 atmosphere. Being ignited in air at 350 °C, the dried gel burnt in a self-propagating combustion way to form a loose powder. After auto-combustion, the combustion product powders were calcined at 500 °C for 3 h to form the desired phase. After that, the product was placed in an ultrasonic irradiation bath at 20 °C for 15 minutes. The influence

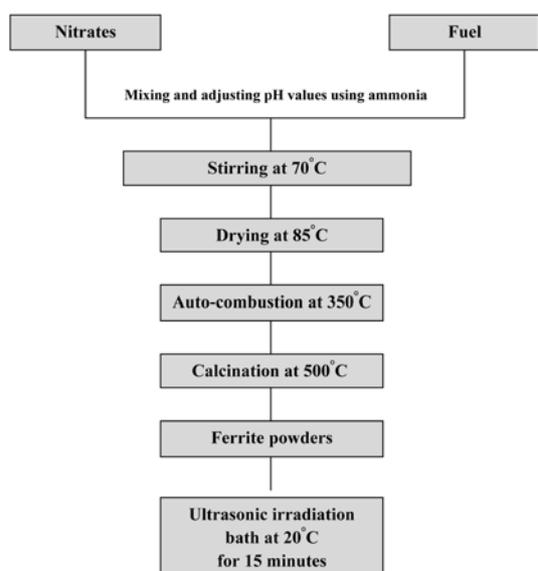


Fig. 1. Flow chart for preparing nanocrystallite ferrite powders by a combination of sol-gel auto-combustion and ultrasonic irradiation methods.

of different pH values in the starting solution on the characteristics of the $CoFe_2O_4$ powder was studied.

Results and Discussion

The experimental observations showed that gels with a molar ratio 1 : 1.2 (nitrates: fuel), exhibit an auto-catalytic combustion behavior. When the gels were ignited, the combustion process rapidly propagated forward until all the gels were burnt out completely to form loose powders. It was also observed that the combustion rate was influenced significantly by the pH value of the mixed solution. With an increase in the pH value from 5 to 9, the combustion rate and the liberated gases increased significantly. The effects of ultrasound radiation on the chemical reactions are due to the very high temperatures and pressures that develop during the sonochemical cavity collapse by acoustic cavitation.

The XRD patterns of the samples are shown in Fig. 2. This shows clearly that a pure spinel ferrite was obtained when the stoichiometric molar ratio of Co and Fe was used. All the samples are single phase ferrites ($CoFe_2O_4$) with cubic spinel structures. The particle size of the

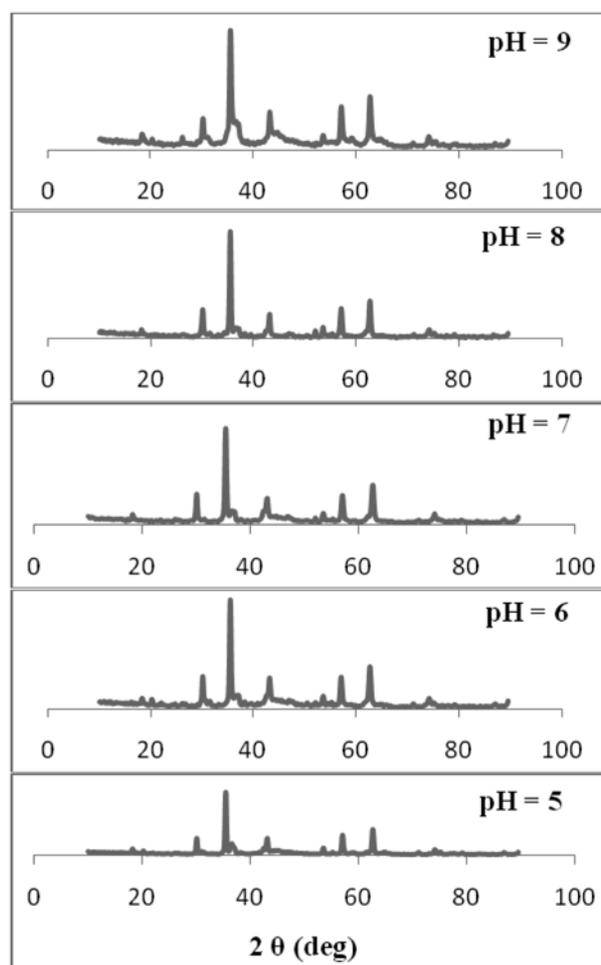


Fig. 2. XRD patterns of samples prepared by sol-gel auto-combustion and ultrasonic irradiation methods with different pH values.

synthesized cobalt ferrite samples were estimated from X-ray peak broadening of the (3 1 1) peak using the Scherrer equation :

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where D is the particle size, λ is the wavelength of Cu $K\alpha$, β is the full width at half maxima (FWHM) of the diffraction peaks, and θ is the Bragg's angle.

The crystallite size for samples prepared at pH 5, 6, 7, 8 and 9 were calculated as 39, 30, 37, 23 and 43 nm, respectively. One of the important factors which can be affect the sol-gel process is the pH value of the solution.

Table 1. Crystallite percent of the $CoFe_2O_4$ phase

pH	5	6	7	8	9
Crystallite percent of $CoFe_2O_4$	43.88	49.89	67.75	44.39	40.48

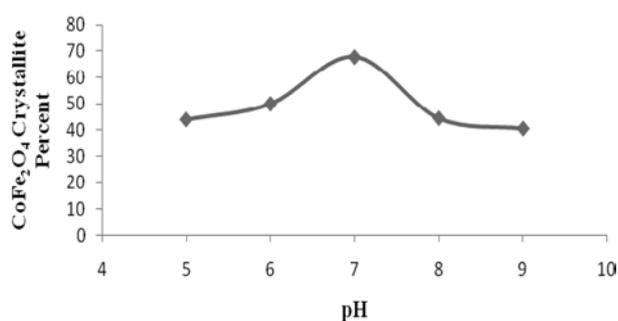


Fig. 3. Influence of the pH value on the crystallite percent.

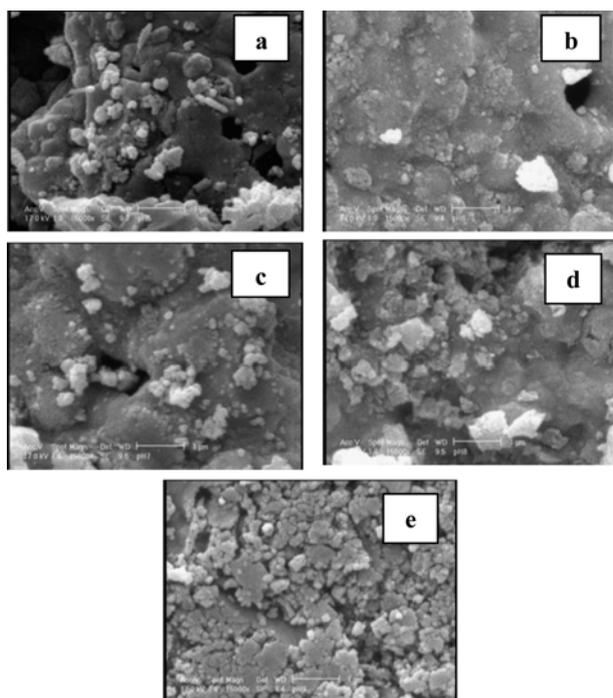


Fig. 4. SEM images of samples prepared at different pH values, (a) pH = 5, (b) pH = 6, (c) pH = 7, (d) pH = 8 and (e) pH = 9.

When the pH value is varied, the crystal size of nanoparticles would be changed. The crystallite percent of $CoFe_2O_4$ phase is presented in Table 1. The influence of the pH value on the crystallite percent of the $CoFe_2O_4$ phase is presented in Fig. 3.

SEM images of samples prepared at pH 5-9 are shown in Fig. 4. These SEM images show that the $CoFe_2O_4$ nanoparticles prepared by a combination of sol-gel auto-combustion and ultrasonic irradiation methods have a uniform, almost spherical structural morphology with a narrow size distribution of particles. The porous feature of agglomerates is attributed to the liberation of a large amount of gas during the combustion. The values of particle sizes from the SEM results are in good agreement with the particle sizes calculated by Scherrer's equation. Energy dispersive X-ray microanalysis (EDAX) results show that no impurities are observed in samples at different pH values (Fig. 5) and EDAX results are given in Table 2.

Information on the chemical changes taking place

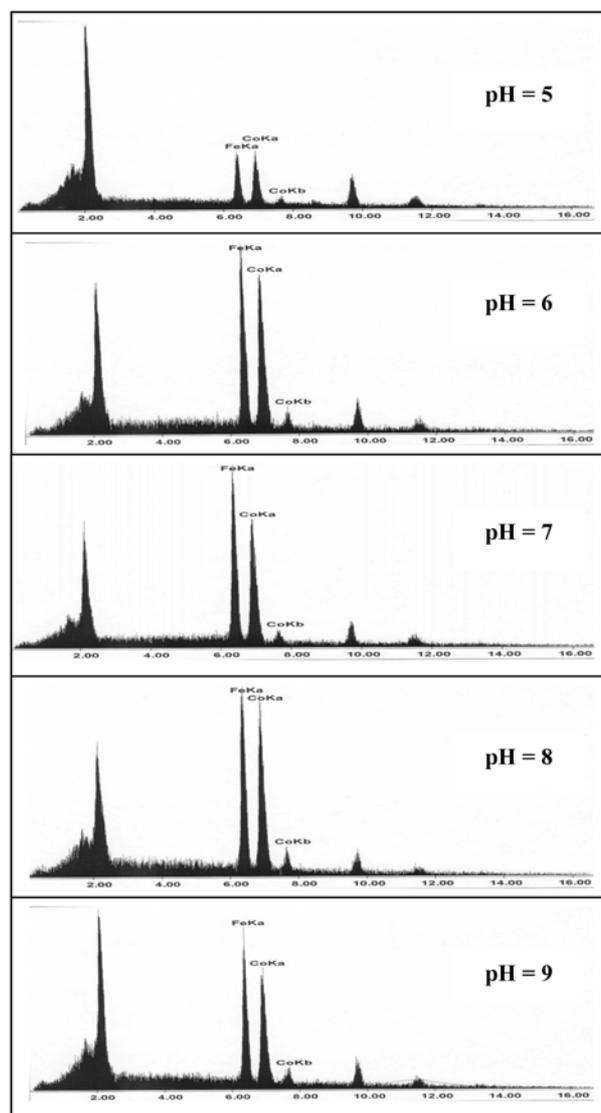
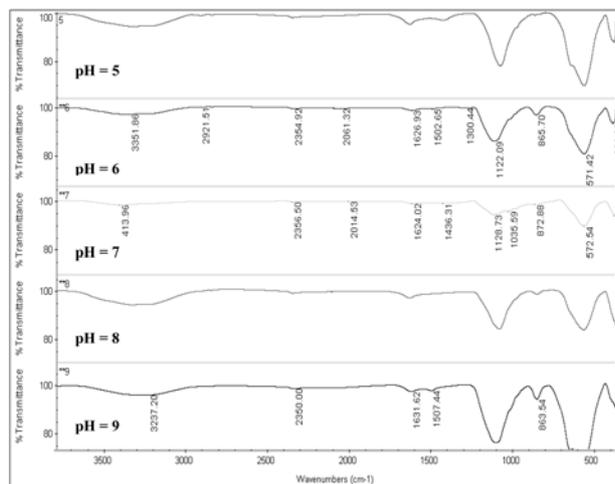
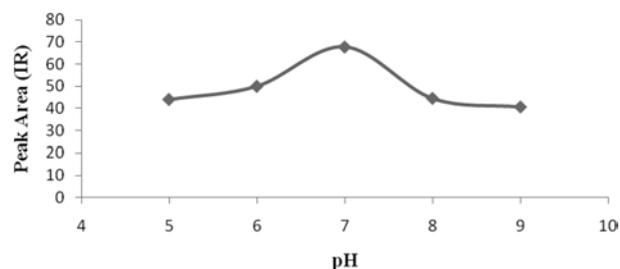


Fig. 5. EDAX analysis of samples prepared at different pH values.

Table 2. EDAX results of nanocrystallites CoFe_2O_4 at different pH values

pH	5	6	7	8	9
Fe_2O_3 (Wt %)	47.92	50.05	55.05	50.99	52.21
CoO (Wt %)	52.08	49.95	44.95	49.01	47.79

**Fig. 6.** IR spectra of the CoFe_2O_4 powders at pH 5-9.**Fig. 7.** The dependence of the band peaking area at about 570 cm^{-1} with pH values.

during the combustion process was obtained by infrared spectral analysis, which would be very helpful for understanding the combustion-related reaction. Fig. 6 shows the FTIR spectra of the CoFe_2O_4 powders at pH 5-9. The scale of wave number is from 400 to 4000 cm^{-1} . Data analysis on the FTIR spectra of ferrite powders indicates that the characteristic band peaking at about 570 cm^{-1} originates from absorption corresponding to the stretching vibrating band of M-O (M = Fe, Co). The magnetic properties would be affected by the external molecular force which can lead to little shift in the vibration band. FTIR spectra results indicate that band peaking at about 570 cm^{-1} confirm the XRD results. The dependence of the band peaking area at about 570 cm^{-1} with pH values is shown in Fig. 7.

Conclusions

Cobalt ferrite (CoFe_2O_4) powders with nanocrystalline

sizes were produced by a combination of sol-gel auto-combustion and ultrasonic irradiation techniques employing a mixture of urea, thiourea and glycine as the fuel (the molar ratio of metal nitrates to fuel was 1 : 1.2). The pH values were changed from 5 to 9. With an increase in the pH value, the combustion rate is increased significantly. All the samples are single phase ferrites (CoFe_2O_4) with cubic spinel structures. The synthesized powders had a particle size distribution in the range of 23-43 nm. The XRD results show that crystallite percent of CoFe_2O_4 phase grows with an increase in the pH from 5 to 7 and then it decreases. The maximum percent of cobalt ferrite crystallites is observed at pH = 7. FTIR spectra results indicate that band peaking at about 570 cm^{-1} is high at pH values 5, 9, then it reduces at pH 6, 8 and at last this peak has the smallest size at pH = 7.

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