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Effect of pH on nanocrystalline Co-ferrite prepared using urea and thiourea fuels by combination of sol-gel auto combustion and ultrasonic irradiation methods

ABSTRACT

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The aim of this study is to evaluate the influence of pH on the synthesis of nanocrystalline cobalt ferrite by combination of sol-gel auto combustion and ultrasonic irradiation methods. Two different fuels, urea and thiourea, along with metal nitrates (oxidant) were used to prepare CoFe_2O_4 powders. The morphology of the resulting powders was investigated. The powders were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Phase pure spinel cobalt ferrite powder was obtained at pH values 6 and 7 after the calcinations at 750°C when urea was used as the fuel; however, the samples obtained using thiourea fuel contained impurities. The average crystalline size was 21 and 37 nm, respectively, for the samples containing urea and thiourea.

Keywords: *Nanocrystalline; CoFe_2O_4 ; Sol-gel auto-combustion; Fuel; Ultrasonic irradiation; XRD; SEM.*

INTRODUCTION

Nanocrystalline ferrites have been extensively studied because of their superior physical and chemical properties compared with bulk counter parts [1, 2]. Among spinel ferrites, cobalt ferrite (CoFe_2O_4) has attracted considerable attention in recent years due to the unique physical properties such as high Curie temperature, large magneto crystalline anisotropy, high coercivity, moderate saturation magnetization, large magnetostrictive coefficient, excellent chemical stability and mechanical hardness [3]. The physical and chemical properties of spinel nanoparticles are greatly affected by the synthesis route. For this reason, various methods have been reported in the literature for the preparation of these nanoscale spinel particles such as ceramic method [4], sol-gel [5], co-precipitation [6], solvent evaporation [7], hydrothermal [8], combustion [9], micro emulsion [10] and citrate methods [11].

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Recently, Sol-gel combustion synthesis is an easy and convenient method for the preparation of a variety of advanced ceramics, catalysts and nanomaterials. In this technique, based on the principles of the propellant chemistry, a thermally induced red ox reaction takes place between an oxidant and a fuel [12]. The crystalline size of the obtained compound in this method can be varied by changing the solution composition, pH effect, and calcinations temperature [13]. Additionally, the reaction is affected by the nature of the organic complexing agent (fuel), the stability of the metal ion complex and the flame temperature of the auto-combustion reaction [14]. Some other advantages of sol-gel combustion are: Simple equipment; High-purity products; Stabilization of metastable phases and Formation of virtually any size and shape products [15].

Ultrasonic cavitation chemistry, an approach for synthesizing a variety of compounds at 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 facile 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 the reduced temperatures [16].

This paper, presented the influence of pH on the synthesis of nanocrystalline-co-ferrite using urea and thiourea flues by combination of sol-gel auto-combustion and ultrasonic irradiation methods followed by calcination at 750°C.

EXPERIMENTAL

Materials and Equipments

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Merck), Urea ($\text{CO}(\text{NH}_2)_2$), Thiourea ($\text{CS}(\text{NH}_2)_2$, Merck) and NH_4OH (Merck) was obtained with analytical grade. All materials were used without further purification. Deionized water was used for all experiments.

X-ray diffraction (XRD) was used to determine the phases and crystalline size. XRD patterns were recorded on a Philips: XPert- MPD with operated at 40 kV / 30mA) diffractometer using Co radiation in 2θ range from 20° to 80° by $0.02^\circ/\text{s}$ step size. The morphology of particles was observed by scanning electron microscopy (SEM) (Phillips XL30 with 16 kV operating voltage). Ultrasonic irradiation (HF-Frequency 35 kHz, 240W) is made in Germany.

Methods; Preparation of cobalt ferrite nanocrystals

Nanocrystalline cobalt ferrite (CoFe_2O_4) was prepared by combination of the sol-gel auto-combustion method using different fuels, urea and thiourea. Appropriate proportion of metal nitrates were taken in the required ratio (molar ratio of $\text{Co}^{3+}/\text{Fe}^{2+}$ was 1:1) and dissolved in deionized water. Then, different fuels (urea and thiourea) were added separately to the mixed nitrate. The molar ratios of fuel (urea and thiourea) to metal nitrates were 3:1. Then, the solutions pH values were adjusted from 5 to 9 with ammonia. The mixtures were stirred until sol formed. In each case the solution was dehydrated slowly at 70°C on a hot plate forming viscous gel. On further heating about 300°C , the temperature gel increased and at a certain temperature auto-ignition of the gel took place and dried gel spontaneously combusted in air to form the loose powders. Finally, the as-burnt powders were calcined in air at 750°C for 4 h with a heating rate of $10^\circ\text{C}/\text{min}$ to obtain cobalt ferrite nanoparticles. Then, the product was placed in ultrasonic irradiation bath at 15°C for 45 minutes. For studies on the effect of pH, ten samples were prepared with pH 5, 6, 7, 8 and 9 is called U_5 , U_6 , U_7 , U_8 and U_9 for urea; T_5 , T_6 , T_7 , T_8 and T_9 for thiourea, respectively.

RESULTS AND DISCUSSION

Phase analysis and crystalline size of products at different pH values

The XRD patterns of the as-synthesized powder urea route (U_5 , U_6 , U_7 , U_8 and U_9) are shown in Figure 1. The peaks are broad indicating nanocrystalline nature of the powders. The crystalline size has been calculated from FWHM

(full width at half maximum) data using Scherrer formula:

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

where D is the particle size, λ is the wavelength of Co $K\alpha$, β is the corrected line width at half peak intensity of the diffraction peaks, and θ is the Bragg's angle. The reflection from (311) plane was used for determination of average crystalline sizes. The calculated average crystalline sizes 19.46, 21.48, 20, 25 and 22.18 nm for U_5 , U_6 , U_7 , U_8 and U_9 samples, respectively. The Phase

analysis diffraction peaks of U_5 , U_8 and U_9 samples confirmed the formation of cobalt ferrite ($CoFe_2O_4$), cobalt oxides (Co_3O_4 and CoO) with structure face centered cubic spinel and $Fd3m$ (227) space group. In both samples of U_6 and U_7 powders single-phase cobalt ferrite has been obtained. The absence of extra reflections in diffraction patterns of as prepared materials ensure phase purity. Average crystalline size (nm), composition of phase and crystalline percent of each for U_5 , U_6 , U_7 , U_8 and U_9 samples are presented in Table 1.

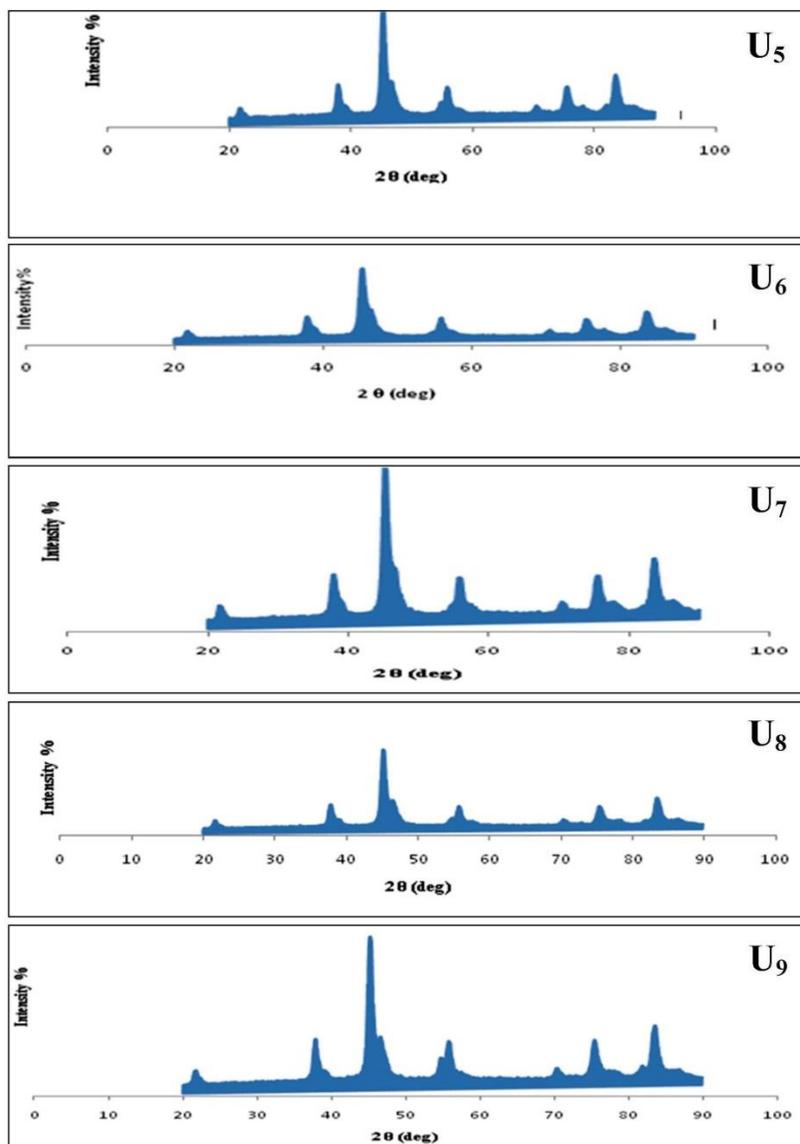


Fig. 1. The XRD patterns of the as-synthesized powder urea route (U_5 , U_6 , U_7 , U_8 and U_9) at different pH from 5 to 9.

Table 1. Composition of phases, average crystalline size (nm) and crystalline percent of each for U₅, U₆, U₇, U₈ and U₉ samples prepared using urea as fuel.

Urea fuel	U ₅	U ₆	U ₇	U ₈	U ₉
Composition of phases	CoFe ₂ O ₄ CoO Co ₃ O	CoFe ₂ O ₄	CoFe ₂ O ₄	CoFe ₂ O ₄ CoO Co ₃ O	CoFe ₂ O ₄ CoO Co ₃ O
Average crystalline size (nm)	19.46	21.48	20	25	22.18
Crystalline percent%	43.89%	34.51%	35.60%	45.07%	45.89%

The XRD patterns of samples (T₅, T₆, T₇, T₈ and T₉) are shown in Figure 2. The calculated average crystalline sizes 38.19, 39, 33, 36.63 and 37 nm for samples T₅, T₆, T₇, T₈ and T₉, respectively. All of the diffraction peaks of samples T₅, T₇ and T₉ are confirmed the formation of cobalt ferrite (CoFe₂O₄) except for sample T₆ and T₈. The XRD patterns of T₅ sample confirmed the formation of cobalt ferrite (CoFe₂O₄), cobalt sulfate (CoSO₄), CoS₂ and ammonium nitrate (NH₄NO₃). Also, cobalt sulfate (CoSO₄), Hematite (Fe₂O₃) and Fe₄(OH)₁₀SO₄ phases were obtained for sample T₆. The Phase analysis diffraction peaks of T₇ sample are confirmed the formation of cobalt ferrite (CoFe₂O₄), cobalt sulfate (CoSO₄) and Fe₄(OH)₁₀SO₄ phases. The Phase analysis diffraction peaks of T₈ sample are presented the formation of cobalt sulfate (CoSO₄), pyrite (FeS₂), Hematite (Fe₂O₃), ammonium nitrate (NH₄NO₃) phases and ammonium chloride (NH₄Cl). Finally, The XRD patterns of T₉ sample confirmed the formation of cobalt ferrite (CoFe₂O₄), cobalt sulfate (CoSO₄), pyrite (FeS₂), Hematite (Fe₂O₃) and ammonium nitrate (NH₄NO₃) phases. Average crystalline size (nm), composition of phase and crystalline percent of each for T₅, T₆, T₇, T₈ and T₉ samples are presented in Table 2.

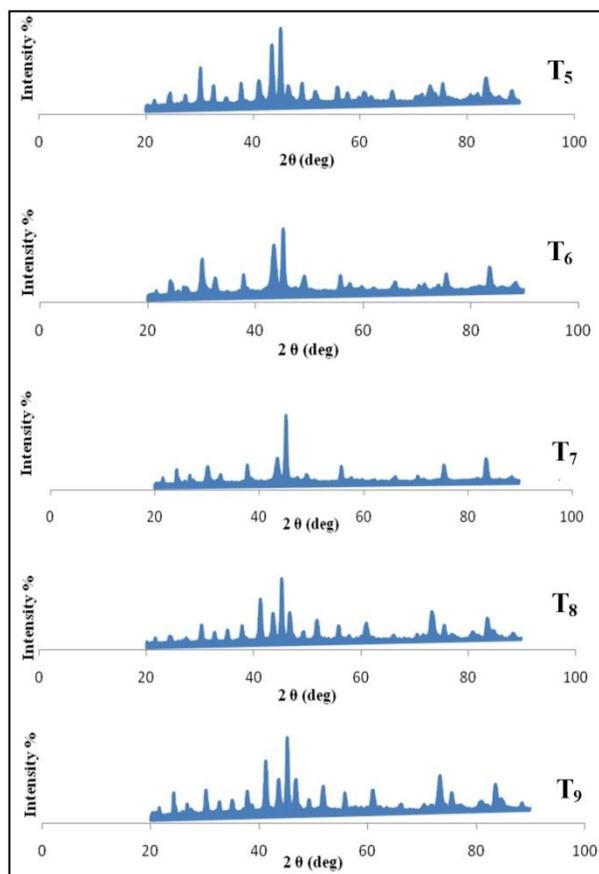
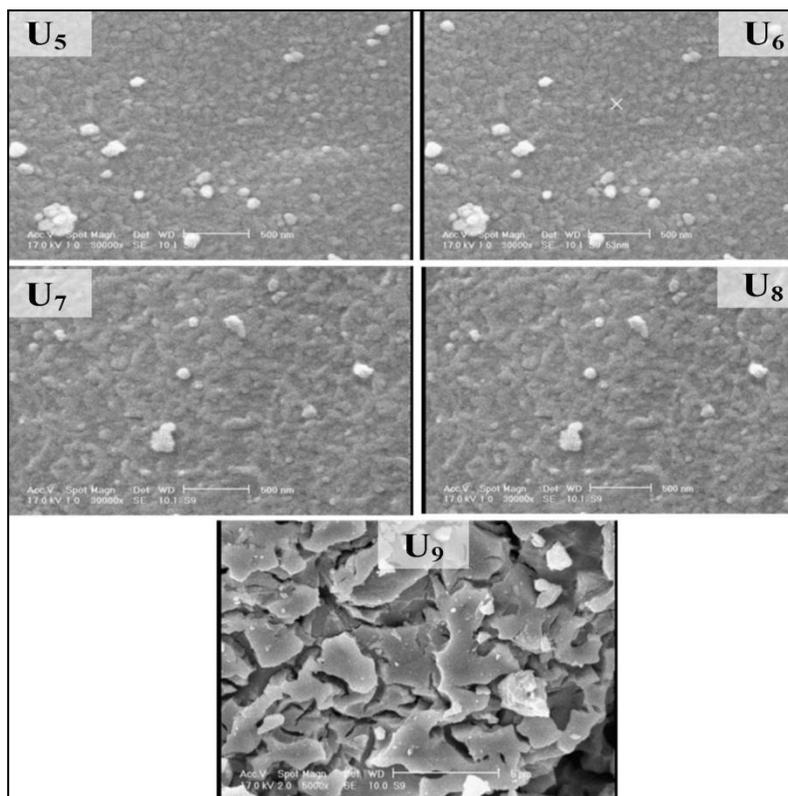
**Fig. 2.** The XRD patterns of samples synthesized powder using thiourea fuel (T₅, T₆, T₇, T₈ and T₉) at different pH from 5 to 9.

Table 2. Composition of phases, average crystalline size (nm) and crystalline percent of each for T₅, T₆, T₇, T₈ and T₉ samples prepared using thiourea as fuel.

Thiourea fuel	T ₅	T ₆	T ₇	T ₈	T ₉
Composition of phases	CoFe ₂ O ₄ CoSO ₄ NH ₄ NO ₃ CoS ₂	CoSO ₄ NH ₄ NO ₃ Fe ₄ (OH) ₁₀ SO ₄	CoFe ₂ O ₄ CoSO ₄ NH ₄ NO ₃ Fe ₄ (OH) ₁₀ SO ₄	CoSO ₄ Fe ₂ O ₃ FeS ₂ NH ₄ NO ₃ NH ₄ Cl	CoFe ₂ O ₄ CoSO ₄ Fe ₂ O ₃ FeS ₂ NH ₄ NO ₃
Average crystalline size (nm)	38	39	33	36.63	37
Crystalline percent%	27%	39.81%	33%	34.43%	27.24%

The SEM images (Figure 3 and 4) for all samples shows that the morphology of particles was almost spherically, regular in shape and dispersed uniformly, but agglomerated to some extent due to the interaction between magnetic nanoparticles, whereas the gel exhibits relatively

porous network. Since this method makes use of the exothermicity of redox reaction, agglomeration commonly exists in the ceramic powders synthesized by sol gel auto combustion method [17].

**Fig. 3.** The SEM images for all samples prepared with urea fuel (U₅, U₆, U₇, U₈ and U₉) at different pH from 5 to 9.

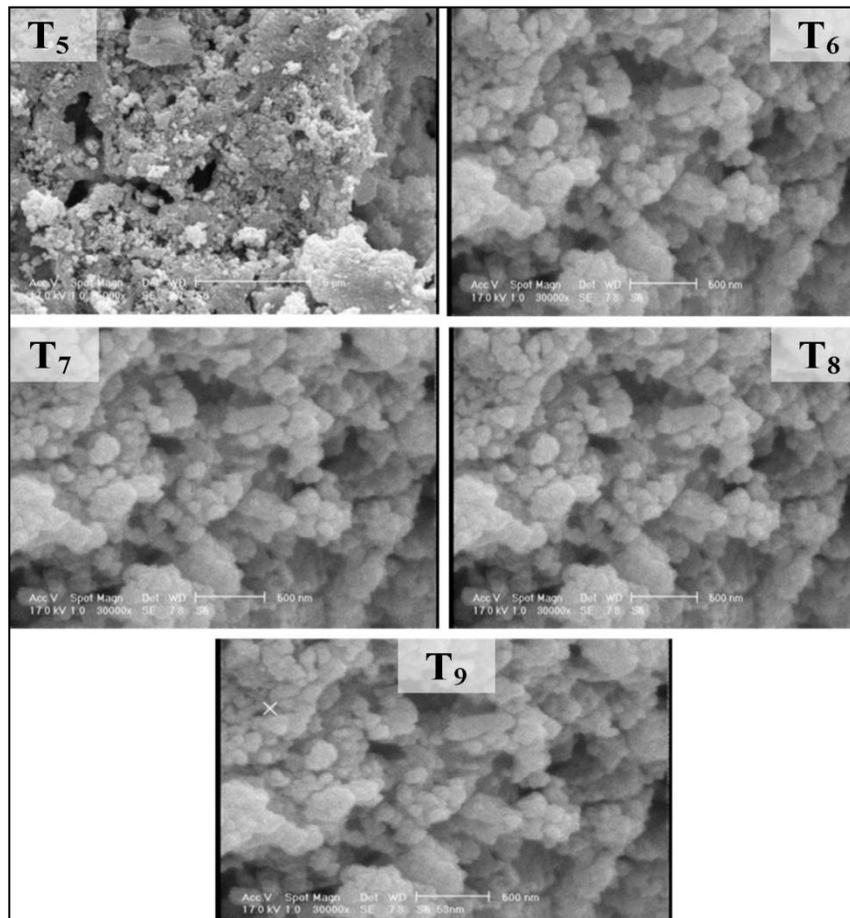


Fig. 4. The SEM images for all samples prepared with thiourea fuel (T_5 , T_6 , T_7 , T_8 and T_9) at different pH from 5 to 9.

CONCLUSION

Nanocrystalline CoFe_2O_4 was prepared using urea and thiourea fuels by combination of sol-gel auto combustion and ultrasonic irradiation methods. The results have shown that, the pH value in the starting solution has a significant influence on the combustion process, crystalline percent, substances (crystalline phases), and size of the as-synthesized powder. Pure spinel cobalt ferrite can be obtained by using only urea as fuel, at pH 6 and 7 with the crystalline size of about 20 nm and uniform in both morphology and particle size due to intense and rapid combustion. Additionally, urea fuel exhibited better powders with high crystalline percent and purity spinel cobalt ferrite phase in comparing with thiourea fuel. In pH values 5 and 8 when thiourea is used as fuel could not form cobalt

ferrite phase. According to these results at pH value 7 average crystalline size obtained by using urea and thiourea fuels decrease.

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