Preparation and Evaluation of NiFe$_2$O$_4$ and CuFe$_2$O$_4$ Nanocatalysts by Combination of Sol- Gel Auto-Combustion Method and Irradiation Technique

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ABSTRACT

The dried nitrate-urea gels exhibit the combination of auto-catalytic combustion behavior and ultrasonic, which can be used to synthesize the nanocatalyst ferrite powders. Cu and Ni ferrites nanocatalyst powders with composition of CuFe$_2$O$_4$ and NiFe$_2$O$_4$ were synthesized by a sol–gel auto catalytic combustion process. The molar ratio between metal ions and urea was 1:1.2. The sol- gel process was done at 80 $^\circ$C. The nanoparticle crystallines have been calcined at 800 $^\circ$C.

Combustion behavior and crystallite size of synthesized powders were investigated with the help of Scanning Electron Microscopy observation and X-ray diffraction technique. X- ray diffraction and Scanning Electron Microscopy were carried out for characterization of the powders. The grain size of the prepared ferrite powders is found to be in the range 30-35 nm.

Keywords: Auto-Combustion; Irradiation Technique; Sol- Gel, CuFe$_2$O$_4$; NiFe$_2$O$_4$; SEM; XRD

INTRODUCTION

The sol- gel method, in particular, is one of the most useful and attractive techniques for the synthesis of nanosized ferrite materials, because of its advantages such as; good stoichiometric control and the production of ultrafine particles with a narrow size distribution in a relatively short processing time at very low temperature. Sol-gel methods generally refer to the hydrolysis and condensation of metal alkoxides or alkoxide precursors, leading to dispersions of oxide particles in a sol. The sol then dried or geled by solvent removal or by chemical reaction. In general, water is used as the solvent, but the precursors can also be hydrolyzed by an acid or basic medium. The catalysis process induces the formation of colloidal as well as polymeric from of the gel [1, 2].

Soft and hard ferrites are a group of technologically

important magnetic materials. One of these ferrites is NiFe$_2$O$_4$. This material is largely used in electric and electronic devices, radar-absorbing coatings, ferro-fluids, and catalysts [3]. Nickel ferrite dominates the corrosion product oxide inventory in pressurized heavy water reactors and hence it plays a major role in the activity transport process [4].

Spinels of the type of M^{2+}M$^{3+}_2$O$_4$ attract the research interest because of their unique properties and multiple applications in various fields [5-8]. Copper ferrite, CuFe$_2$O$_4$, is one of these compounds. Several methods have been employed to prepare copper ferrite, such as, sol–gel method [9-14], co- precipitation [15-19], solid state reaction [20] and auto - combustion

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[21]. Combustion synthesis processes are characterized by high-temperatures, fast heating rates and short reaction times. These features make CS an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes. In solid state combustion (SSC), initial reactants, inter-mediates and final products are all in the solid state. Combustion of solid reactants can occur in two modes: (i) Linear or self-propagating, high temperature synthesis (SHS) and (ii) bulk or volume combustion synthesis (VCS) [22].

For solid-state synthesis, it is difficult to achieve uniformity of product and needs higher synthesis temperature and longer sintering time [23]. Compared with solid-state synthesis, the co- precipitation method makes the materials react uniformly at molecular level and has the advantages of lower polycrystalline-synthesized temperature and shorter sintering time [24 - 26]. The results show that the nanometer $CuFe_2O_4$ has high a catalytic activity. In this study, $CuFe_2O_4$ and $NiFe_2O_4$ nanocatalysts was synthesized by combination auto- combustion and irradiation beam technique.

EXPERIMENTAL

$CuFe_2O_4$ and $NiFe_2O_4$ nano powders were prepared by sol-gel method. (Cu $(NO_3)_2 \cdot 3H_2O$, Merck), (Ni $(NO_3)_2.6H_2O$, Merck), (Fe $(NO_3)_3 \cdot 9H_2O$, Merck), (urae), Merck) and NH_4OH (Merck) were used as raw materials. All the reagents were used without further purification. X-ray diffraction (XRD) patterns of nanopowders were obtained with an X-ray diffractometer (Model: XPERT-MPD, Philips) using Cu Kα radiation (λ=1.5406 ^oA) with operated at 40 kV and current of 40 mA. The shape and morphology of powder were analyzed by Scanning Electron Microscopy (SEM- Phillips XL 30). The HF-Frequenz 35 KHz, 240 w / Made In Germany was used as ultrasonic bath at 15 ^oC.

Appropriate amounts of ferric, nickel and copper nitrates and thiourea, were first dissolved in a minimum amount of deionized water. The molar ratio of nitrates to thiourea was 1:2. A small amount of ammonia was added to the solution to adjust the pH value at about 10. During this procedure, the solution was continuously stirred using a mechanical agitator.

Then, the mixed solution was poured in to a dish and heated and stirred constantly to transform it into a xerogel. When ignited points were observed, the dried gel burnt in a self-propagating combustion manner until all the gel was burnt out completely to form a loose powder. The powder was then calcined at 800 ^oC for 4 h. In orther hand, to prepare monodisperse $CuFe_2O_4$ and $NiFe_2O_4$ nanoparticles, the powder was dispersed by ultrasonic technique for 15 minutes.

RESULTS AND DISCUSSION

The XRD patterns of the Cu and Ni ferrites nano crystalline powders are shown in Fig.1. The particle size of the samples has been determined employing the Scherrer equation:

$$D = k\lambda / \beta\cos\theta \qquad [1]$$

Where β is the full width half maximum (rad), λ the wavelength of the X-ray, θ the angle between the incident and diffracted beams (degree) and D the particle size of the sample (nm). The results of XRD show at lower temperature the diffraction lines have confirmed the formation of single phase of spinel ferrite $NiFe_2O_4$ nanoparticles and for nanopowders of CuFe2O4 were observed composition of phases $CuFe_2O_4$, CuO and Fe_2O_3.

The nanoparticles structural of $CuFe_2O_4$ are Tetragonal, Monoclinic, Rhombohedral, and for $NiFe_2O_4$ is Cubic. The grain sizes of the prepared ferrites are found to be in the range 30- 35 nm.

The structural morphology of the nanoparticles was investigated using Scanning Electron Microscopy (SEM). Fig. 2, shows the SEM images of $CuFe_2O_4$ and $NiFe_2O_4$ nanocatalysts.
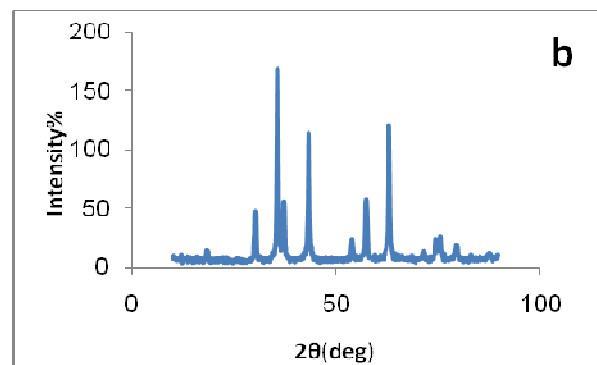

Fig. 1. The XRD patterns for $CuFe_2O_4$ (a) and $NiFe_2O_4$ (b) ferrite nanocatalysts powder.
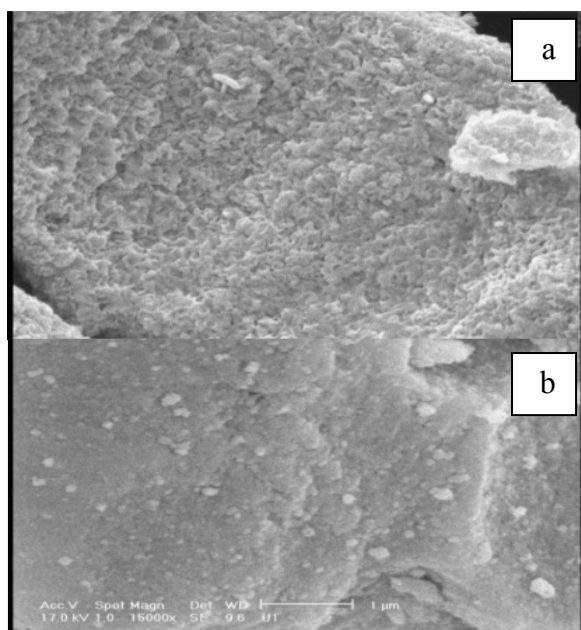
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Fig. 2. SEM images of nanoparticles for a) $CuFe_2O_4$ and b) $NiFe_2O_4$.

CONCLUSION

A nitrate- urea gels were prepared from metal nitrates and fuel by a sol- gel auto- combustion process in order to synthesize $CuFe_2O_4$ and $NiFe_2O_4$ ferrites. The well- crystalline copper ferrite and nickel ferrite was produced when pH = 10. So, it is necessary to adjust appropriate pH to produce pure copper ferrite and nickel ferrite. The grain sizes of the prepared ferrites are found to be in the range 30- 35 nm. The particles have been calcined at 800 °C for 4 h. Then the products were placed in ultrasonic bath of n-butanol for 15 minutes. SEM results showed that the grains were regular sphere-shaped nanoparticles. The XRD data show nanocatalyst powders have phases for $CuFe_2O_4$: $CuFe_2O_4$, CuO and Fe_2O_3 and for $NiFe_2O_4$: $NiFe_2O_4$.

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