Journal of University of Babylon, Engineering Sciences, Vol.(26), No.(4): 2018.

The Effect of Catalyst Type on The Microstructure and Magnetic Properties of Synthesized Hard Cobalt Ferrite Nanoparticles.

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Abstract

A sol-gel process prepared the nanoparticles of hard cobalt ferrite ($CoFe_2O_4$). Cobalt nitrate hexahydrate ($Co\ (NO_3)_2{\cdot}6H_2O$), iron nitrate nonahydrate ($Fe\ (NO_3)_3{\cdot}9H_2O$) with using two catalysis acid (citric acid) and alkaline (hydroxide ammonium) were used as precursor materials. Crystallization behavior of the $CoFe_2O_4$ nanoparticles were studied by X-ray diffraction (XRD). Nanoparticles phases can change from amorphous to spinel ferrite crystalline depending on the calcinated temperature at 600°C, with using citric acid as a catalysis without finding forgone phase, while using hydroxide ammonium was shown second phase (α-Fe_2O_3) with $CoFe_2O_4$. Crystallite size was measured by Scherrer's formula about (25.327) nm and (27.119) nm respectively. Structural properties were investigated by FTIR, which was appeared main bond of (Fe-O), (Co-O), (C-O), and (H-O). Scanning electron microscopy (FE- SEM) was shown the microstructure observation of cobalt ferrite and the particle size at the range about (28.77-42.97) nm. Magnetization measurements were carried out on a vibrating sample magenometer (VSM) that exhibited hard spinel ferrite.

Key words : Nanoparticles, Ferrite, Sol- gel, cobalt, Acid, Alkaline, FE-SEM, XRD, VSM, FTIR.

الخلاصه

تم تحضير الجسيمات النانوية من الكوبالت الفرايت الصلب ($CoFe_2O_4$) بواسطة عملية سول–جل. نترات الكوبالت المائية ($Co\ (NO_3)_2{\cdot}6H_2O$)، ونترات الحديد المائية ($Fe\ (NO_3)_3{\cdot}9H_2O$) باستخدام اثنين من المحفزات: محفز حامضي (حمض الستريك) ومحفز قلوي (هيدروكسيد الأمونيوم). تم دراسة السلوك البلوري لجسيمات الفرايت النانوية بواسطة حيود الأشعة السينية. يمكن أن يتغير تركيب الجسيمات النانوية من الفرايت العشوائي إلى الفرايت السبينل البلوري اعتمادا عند درجة حرارة حرق 600 درجة مئوية، مع استخدام حامض الستريك كمحفز تم الحصول على طور $CoFe_2O_4$ مفرد نقي دون وجود أي اطوار ثانويه، في حين عند استخدام الأمونيوم هيدروكسيد كمحفز ظهر وجود الطور الثانوي(α-Fe2O3) مع $CoFe_2O_4$. اما قطر البلورة فتم حسابها بواسطة معادلة شيرر Scherrer's formula وكان حوالي (25.327) نانومتر و (27.119) نانومتر على التوالي. دراسة الخصائص التركيبة تمت بواسطة فحص FTIR والتي ظهرت ارتباط رئيسي (O–Fe) و (O–Co) و (C-O) و (H-O). أظهر المسح المجهري الإلكتروني (FE-SEM) الخصائص التركيب الهيكلي للكوبالت الفرايت وحجم الحبيبي حوالي (42.97–28.77) نانومتر. اما القياسات المغناطيسية نفذت بواسطة مقياس الاهتزاز المغناطيسي (VSM) والتي أظهرت وجود الفرايت السبنلي الصلب.

الكلمات المفتاحية: الجسيمات النانوية، فرايت، سول – جل، كوبالت، حامض، قلوي، تحليل الاشعة السينية، المجهر الالكتروني الماسح.

1- Introduction:

Ferrites have formed of a ceramic material and iron oxide; ferrites have characterized by dark gray or black color, very hard and brittle. They are synthesized via heat-treating the different transition metal oxides or alkaline earth oxides with the ferric oxides. Ferrite exhibits ferrimagnetisms because of the super-exchange interaction between electrons of metal and oxygen ions (Snoek, 1977). The advantage of ferrites is their high efficiency, low cost and easy to manufacture. The basic electrical and magnetic properties of ferrites are that, they are sensitive to methods of preparation and associated parameters, type and amount of dopant, and the distribution of cations over the available sites. The selection of dopant is also important criteria in governing the properties of ferrite materials (Mund *et.al.,* 2012). Ferrite has classified as “soft” and “hard” ferrite. Soft ferrite has low coercivity, but when high coercivity called the hard ferrites (Rahul, 2012).

Cobalt ferrite has categorized into a hard magnet because it had high values of coercivity, good chemical and physical stability it can be used for different applications. Cobalt ferrite ($CoFe_2O_4$) has a spinel or an inverse spinel structure. It had partially inverse spinel structure, a value of coercivity about 1000 Oe and average magnetization (Ms) about 50 emu/g. Because of its high coercivity, they become a perfect for many magnetic applications: using in high-density materials of magnetic storage, magneto-mechanical, torque sensors in computers, devices for recording, and cards of magnetic (Rahul, 2012). Sol- gel method is considered a common method to produce cobalt ferrite powder since this method can yield a high purity powder with fine particle sizes; also, this method requires a low synthesis temperature. However, the main drawback of this method is low yield (Cernea, 2005). There are many studies and researches, K.Maaz.et al, have synthesized cobalt ferrite nanoparticles by wet chemical process. The salts of cobalt and stable ferric with oleic acid using as precursor materials. The result was shown formation nanoparticles of cobalt ferrite as single phase with grain size in range (15-48) nm. The particle size was increased with raising the annealing temperature and time while the obtained the maximum coercivity peaking at around 28nm (Maaz *et.al.,* 2007). Mahmoud Goodarz Naseri, et al, have synthesized spinel cobalt - ferrite nanoparticles by using a thermal treatment process employing cobalt nitrate and iron nitrate as precursors, PVP also used as an capping agent of agglomeration, while the solvent was deionized water. Sizes of particle between (12.5–39) nm have obtained after heating at calcination temperatures (350 and 650) °C. The results have shown that saturation magnetization (Ms), and remnant magnetization (Mr) of the $CoFe_2O_4$ nanoparticles increased with increasing calcination temperatures (Mahmoud *et.al.,* 2010). Anuchit Hayek et al, have prepared Single-phase of cobalt ferrite ($CoFe_2O_4$) was synthesized with a sol-gel reaction between cobalt nitrate and iron nitrate using polyvinyl alcohol (PVA). Their magnetic coercive field were slightly reduced with the increase in the annealing at 800°C from 2 h to 6 h. After annealing for 4 h, $CoFe_2O_4$ samples from different batches exhibit variations in the magnetic properties. The coercive field has a large distribution because of its sensitivity to the particle agglomeration (Anuchit *et.al.,* 2013). Mahboubeh Houshiar et al, have prepared nano cobalt ferrite ($CoFe_2O_4$) by using three different methods: combustion, coprecipitation, and precipitation. Particle size has shown an average size about 69.5 nm for combustion. These results have shown that three methods may lead to different magnetic properties. The combustion method had Hc and Ms are greatest while the least in precipitation method (Mahboubeh *et.al.,* 2014). C. Murugesan et al, have synthesized $CoFe_2O_4$ by using two processes: first low temperature auto combustion and second high temperature ceramic. Two techniques were differed in methods of preparation and size of the grains due to important changes in electrical and magnetic characterizations. The lattice constant of crystals prepared by low temperature auto combustion was higher than the ceramic method (Murugesan *et.al.,* 2014). A.E Segneanu et al, have prepared magnetic nanoparticles (MNPs) of cobalt-ferrite ($CoFe_2O_4$) as an inorganic-organic hybrid material for biomedical potential application. Sol-gel process and treated at (200 °C) have used to obtain a small peptide. The final nanoparticles have given good potential application in biomedicine (Segneanu *et.al.,* 2014). H.B. Sharma.et al, have prepared nano - cobalt ferrite by using sol-gel auto combustion technique. The results were appeared the average grain size was found to raise from (42 to 95) nm with increasing the amount of citric acid. The dielectric constant increased with increasing in the molar ratio of metal nitrate to citric acid amount (Sharma *et.al.,* 2014). R. Adrian Bortnic et al, 2016, have prepared $CoFe_2O_4$ nanoparticles by using a sol-gel combustion technique. The grain size of nanoparticles about (20-70) nm, which prepared via using hydrated nitrates of iron and cobalt, sucrose and pectin. The pectin addition, simplified form a hard gel from precursor solution through the drying process at (200°C). The black nanopowder has obtained after a calcination process at temperature (700 °C) (Adrian *et.al.,* 2016).

This search focuses on preparation of the hard ferrite in nanoscale. Many applications of the ferrite at microscale have many problems like high leakage current, small remnant polarization, high coercive field, inhomogeneous magnetic spin structure. In addition to the problems in synthesis steps, it has a long time of preparation, difficult manufacturing process, and high calcination temperature. The goal of using the sol - gel technique is to synthesize nanoparticles of hard ferrite with using acid or alkaline medium.

2. Experimental Procedure

2.1 Raw Materials

The starting materials used in this study are presented in table (2.1).

Table (2.1) Starting Materials Used

Starting materials	**Formulation**	**Molecular weight (g/mol)**	**Purity%**	**Physical state**
Iron (III) nitrate nonahydrate	**$(Fe(NO_3)_3 \cdot 9H_2O)$**	**404**	**99**	**Solid**
Cobalt nitrate hexahydrate	**$(CO(NO_3)_2 \cdot 6H_2O)$**	**235**	**99.5**	**Solid**
citric acid	**$(C_6H_8O_7)$**	**192**	**99.5**	**Solid**
Ammonium hydroxide	**NH_4OH**	**35**	**99.9**	**Liquid**

2.2 Preparation cobalt ferrite ($CoFe_2O_4$)

The procedure of this research contains the mixing of ferric nitrate $(Fe(NO_3)_3 \cdot 9H_2O)$ with cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O)$ in a ratio (2:1) with the addition of the distilled water in a 250 ml size beaker. Purpose of producing a homogeneous solution and ensure that the entire materials have been dissolved; the mixing process was conducted using hot plate magnetic stirrer type (Stuart SB 162-3, England) at a temperature 50 °C for 2 hours. The first samples prepared by adding 4.8M (10ml) solution of citric acid to solution of (ferric nitrate & cobalt nitrate) as continuous drops via burette (PH<1). It is mixing using the magnetic stirrer, after 9 hours at 60-70 °C the precursor is transformed into gel form. The second samples prepared by adding alkaline (10 ml) ammonia hydroxide to the first solution of (ferric nitrate & cobalt nitrate) as continuous drops via burette. To the extent that it does not exceed (PH < 9) and mixing by using the magnetic stirrer and the gel is formed after 3 hours at 60-70 °C. Leaves the gel for 12 hours, and then washed twice with distilled water using filtration paper measuring 42. The chemical reactions was happened during preparation step are:

For acid catalyst:

$$Co\,(NO_3)_2{\cdot}6H_2O + Fe\,(NO_3)_3{\cdot}9H_2O + C_6H_8O_7 \longrightarrow$$

$$CoFe_2O_4\,(s) + 28\,H_2O\,(g) + 4N_2\,(g) + 6CO_2\,(g) + 11/2\,O_2\,(g) \quad \ldots (1)$$

For alkaline catalyst:

$$Co\,(NO_3)_2{\cdot}6H_2O + Fe\,(NO_3)_3{\cdot}9H_2O + NH_4OH \longrightarrow$$

$$CoFe_2O_4\,(s) + 25\,H_2O\,(g) + 4N_2\,(g) + 10O_2\,(g) + NH_3\,(g) \quad \ldots (2)$$

After preparing the samples of cobalt ferrite ($CoFe_2O_4$) by the sol-gel method, the next step is drying that gel of ($CoFe_2O_4$) by using porcelain basin at 200°C for 3h in oven dryer type (memmert Gmbh+Co.KG, universal oven (UIS), Germany). Finally the calcination process is followed the drying process, which is done at 600 ºC, with heating rate was kept at 5ºC / min and socking time 3 hours in the air in the furnace up to 1600°C for pyrolysis, type (Protherm, Turkey).

2.3 Characterizations:

The structure of cobalt ferrite ($Cofe_2O_4$) nanoparticle via a sol-gel process has characterized by the diffraction of X-ray (XRD), type (Shimadzo, XRD6000, diffractometer, Japan). X-rays are generated using Copper (Cu-Kα) radiation at 30 kV, 40 mA and wavelength (λ = 1.5406 Å), radiation to generate diffraction patterns from powder samples at room temperature in a 2θ range of 20° to 80°. Fourier Transmission Infrared Spectroscopy (FTIR), type (Iraffinity- 1Shimadzu) model, has done to investigate the main bonds and the ions structure of the crystal, [XRD and FTIR tests done in Materials Engineering College laboratories - university of Babylon]. The microstructure and particle size of the nanocrystals have investigated via scanning electron microscopy (FE-SEM), type (MIRA3 TESCAN- RMRC) (TM - 1000 Hitachi tabletop Japan). Magnetization measurements are doing by using a vibrating sample magnetometer (VSM), model (Mdkft), type (Danesh-pajoohe kashan Co. - Iran), at room temperature, [FE-SEM and VSM test done in Al Raced Laboratory, Tehran – Iran].

3- Results and Discussion:

3.1. XRD Analysis:

XRD can be used to describe the nanoparticles crystallinity. Fig. (1) Shows XRD patterns of cobalt ferrite ($CoFe_2O_4$) nanopowder samples after being calcined at 600 ºC for 3 hours, comparing with the standard JCDPS card. XRD patterns of cobalt ferrite ($CoFe_2O_4$) powder prepared by using citric acid or ammonium hydroxide as a catalyst as shown in Figs. (1) and (2). Observed diffraction peaks matches well with JCPDS cards: No. 022-1086 $CoFe_2O_4$. The diffraction peaks of (220), (311), (222), (400), (422), (511), (440), and (533) characterized the cobalt ferrite phase of spinel. For the first sample (using acid), the only phase appear in all the prepared samples. No foreign phases are detected, proving the phase purity of the samples. While, the second sample (using alkaline) in addition to major peaks the second phase (α-Fe_2O_3) appeared in (012), (104), (113), (024), and (300). This is a residual material that needs high temperatures may be considered secondary phase because the ammonium hydroxide delays the crystalline transformation of a complete transformation requires a higher heat treatment up to 1200°C (Raghvendra, 2016).

The crystallite size was identified by XRD for structural limitation and evaluation of crystalline size by using Scherrer’s formula at the peak (311):

$$D_{XRD} = 0.89\ \lambda / \beta \cos\theta \qquad \ldots (3)$$

Where λ is wavelength of X-ray radiation used in Å, θ is the diffraction angle, β is the full width at half maximum (FWHM) in radians in the 2θ scale, D_{XRD} is the crystallite size in nm (Cullity, 1967).

The lattice parameter of the prepared nanoparticles sample, according to the cubic crystal structure was calculated from the main peak of spinel structure (311) using equation:

$$a = d\sqrt{h^2 + k^2 + l^2} \qquad \ldots (4)$$

where “d” is the interplanar distance, “h, k and l” are the miller indices and “a” is the lattice parameter (Fultz & Howe, 2013). The structural parameters calculated from the diffraction pattern as shown in Table 2.

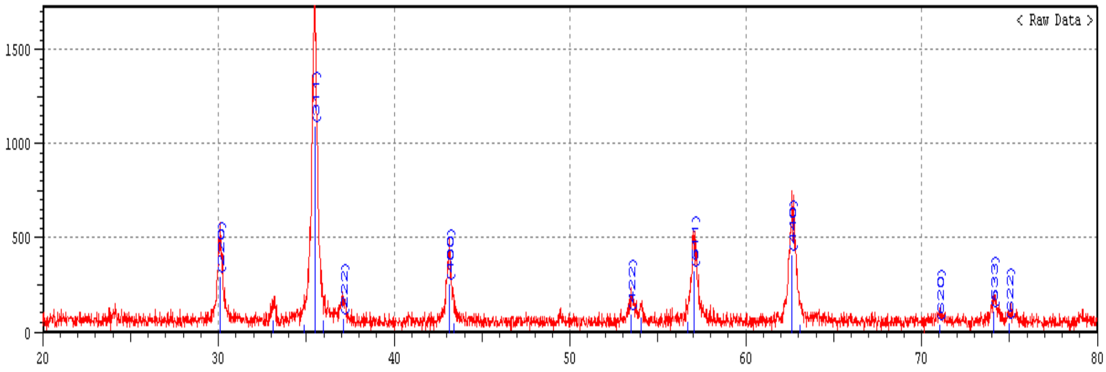

Figure (1): XRD Patterns of Cobalt Ferrite by Acid Calcined at 600 °C

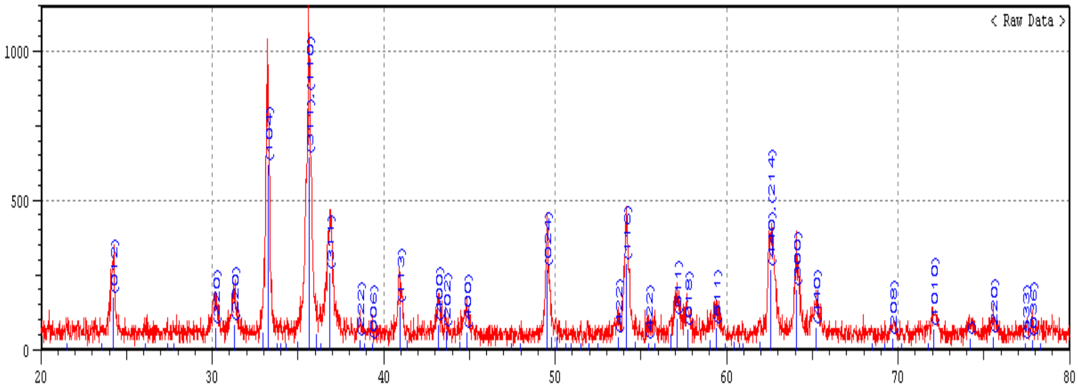

Figure (2): XRD patterns of Cobalt Ferrite by Ammonium Hydroxide Calcined at 600 °C

Table (2) Structural parameters of $CoFe_2O_4$ calcinated at 600°C.

$CoFe_2O_4$	D_{XRD} (nm)	a (Å)
citric acid catalyst	25.3268	8.38377
ammonium hydroxide catalyst	27.119	8.37934

3.2 Fourier Transmission Infrared Spectroscopy (FTIR)

The (FTIR) spectrum represents the ions position in the structure of crystals and their vibration modes. The samples of cobalt ferrite ($CoFe_2O_4$) powder prepared using citric acid or alkaline as a catalyst after being calcinated at 600 °C for 3 hours as shown in Figs (3),(4). The position of spinel ferrite finds in the region of 400–600 cm^{-1} by (Co-O) and (Fe-O) stretching vibration. These bonds are typically related to the pure cobalt ferrite nanoparticles (Patil *et.al.*, 2014). (C-O) bending vibration is monitored at (2310-2380) cm^{-1}. The frequency of the broad peak about (3450–3550) cm^{-1} is referred to (O–H) of the water molecules stretching vibrations. Furthermore, the secondary phase of Fe_2O_3, which appeared in the second sample, is attributed to (Fe-O) in the region, (659.66 – 1627) cm^{-1} corresponds to the stretching vibration (Vinay *et.al.*, 2015).

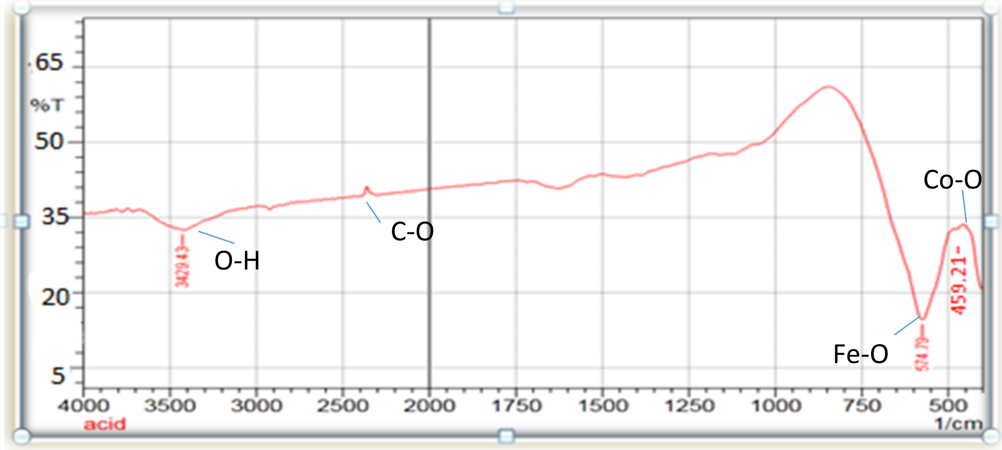

Figure (3) FTIR for Cobalt Ferrite by Acid and Calcined at 600°C

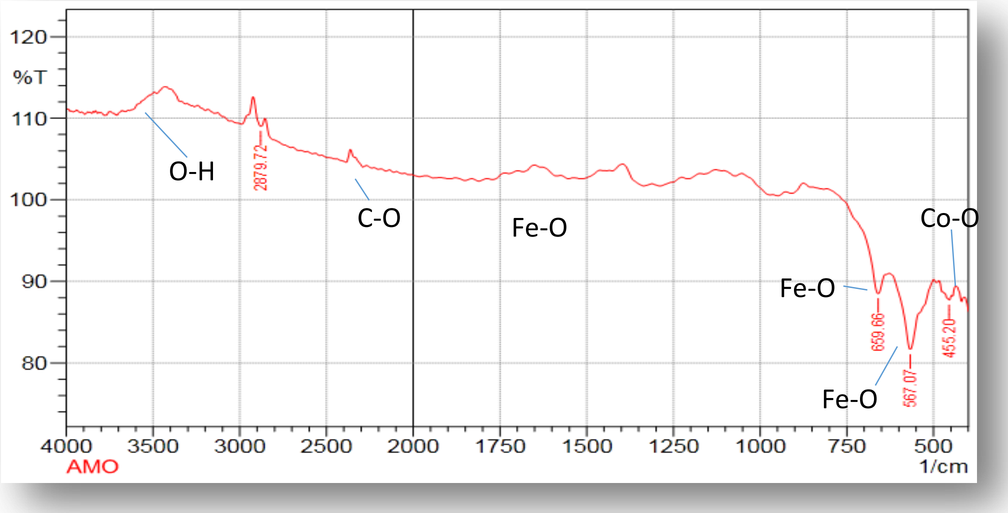

Figure (4) FTIR for Cobalt Ferrite by Ammonium Hydroxide and Calcined at 600°C

3.3 Scanning Electron Microscopy (SEM) analysis.

The structural morphology of nanoparticles was investigated through SEM. Figs (5) and (6) show the SEM images show that nanoparticles of $CoFe_2O_4$ synthesis by a sol-gel process with using citric acid and ammonium hydroxide as a catalyst after calcination at (600 °C) for 3 hours have a uniform spherical structure morphology with a narrow size distribution of particles. Some moderately agglomerated particles as well as separated particles are also present in the images. The grain size was found ranges from (28.77-42.90) nm and (30.16-42.97) nm respectively.

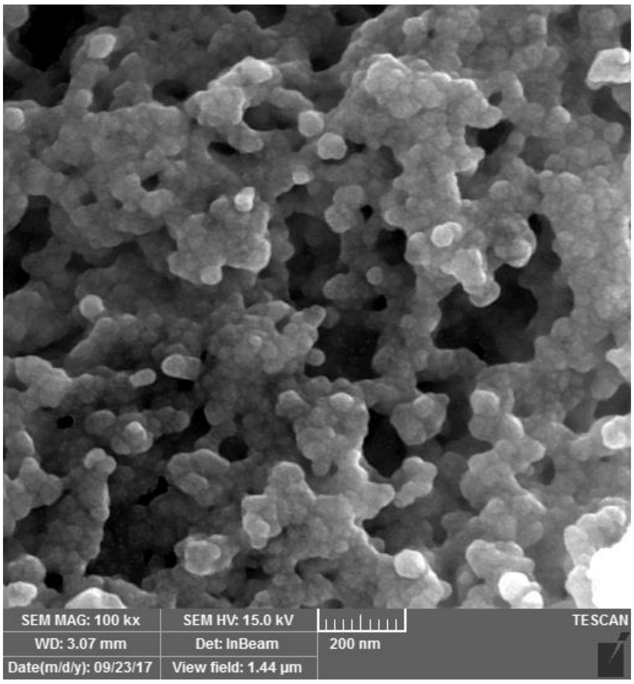

Figure (5) SEM Pattern of Cobalt Ferrite Powder by Acid Calcined at 600°C

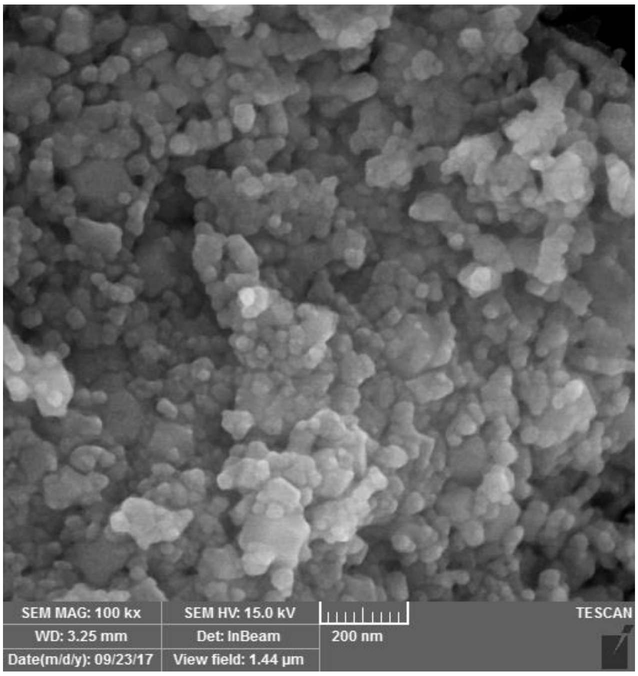

Figure (6) SEM of Cobalt Ferrite Powder by Ammonium Hydroxide Calcined at 600°C

3.4 Vibrating Sample Magnometer (VSM) measurement

The magnetic properties of the $CoFe_2O_4$ nanoparticles were measured through a vibrating sample magnetometer (VSM) with maximum applied field of 9,000 Oe at room temperature. Figs (7) and (8) show magnetic hysteresis loops of nano- cobalt ferrite ($CoFe_2O_4$) synthesis by sol-gel with adding citric acid and ammonium hydroxide as a catalyst after calcination at (600 °C) for 3 hours exhibited hard spinel ferrite. First sample (using acid) the saturation magnetization (Ms), remanent magnetization (Mr) and coercive field (Hc) of the sample were found to be 50 emu/g, 21 emu/g and 1100 Oe, respectively. The high coercivity value of our sample indicates that the particles formed are indeed single domain with no magnetic impurities. Second sample (using alkaline) (Ms), (Mr) and (Hc) of the sample was being 9 emu/g, 5 emu/g and 1320 Oe, respectively. Low value of the saturation magnetization (Ms) due to incomplete crystallization and presence of secondary phases compared with first sample.

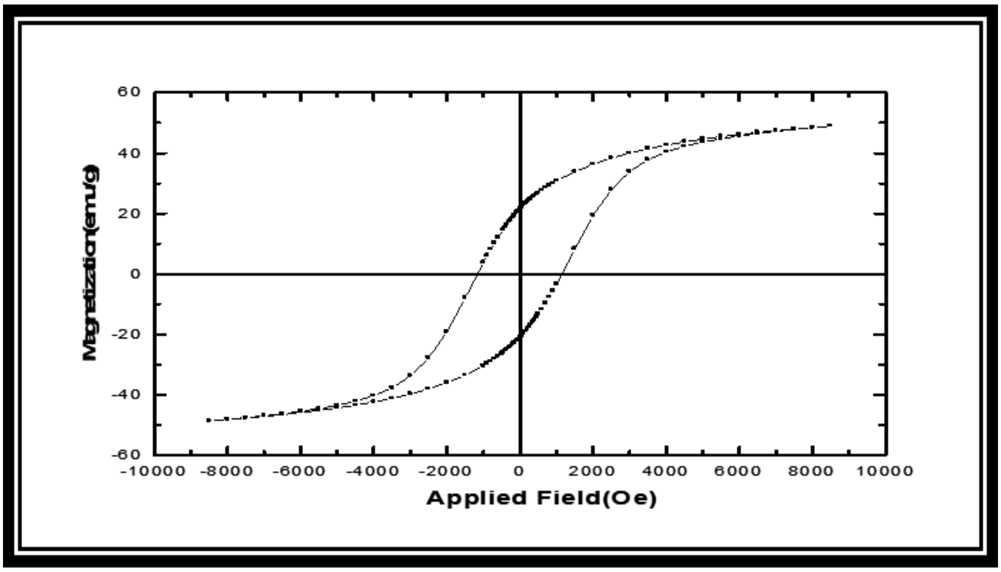

Figure (7) Hysteresis Loop of Cobalt Ferrite by Acid Calcined at 600 °C

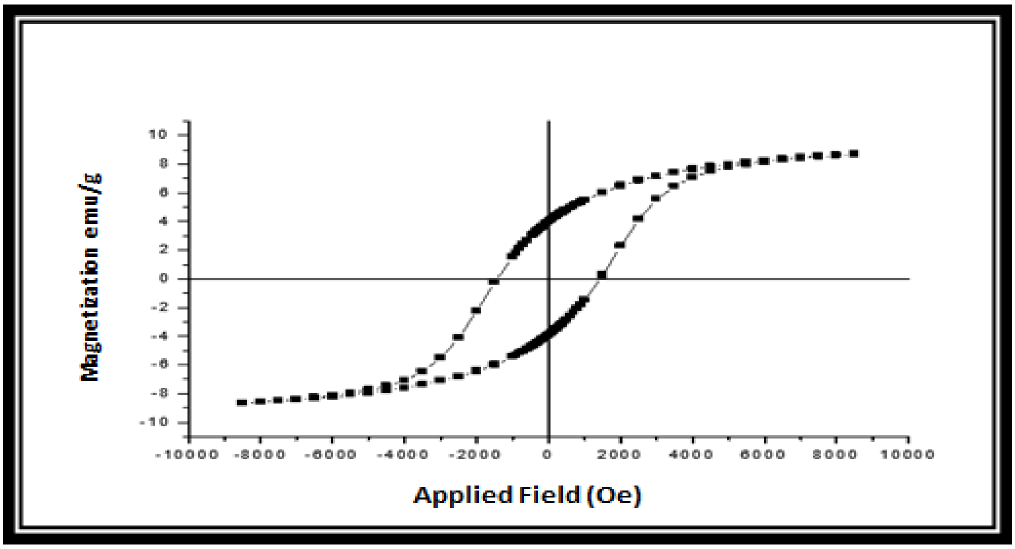

Figure (8) Hysteresis Loop of Cobalt Ferrite by Ammonium Hydroxide Calcined at 600 °C

4. Conclusions

The hard cobalt ferrite $CoFe_2O_4$ nanoparticles have been prepared via the sol-gel process at low calcinations temperatures with a cubic spinel structure and the particle size in the range (17-42) nm. This work focused on the effects of uses acid and alkaline as a catalyst in the preparation of cobalt ferrite nanoparticles and their effect on the variation of properties. Using the alkaline (ammonium hydroxide) as a catalyst leads to a secondary phase of (α-Fe_2O_3), being an impurity in the ($CoFe_2O_4$) produced compared with used acid (citric acid) as a catalyst that no foreign phases are detected. The magnetic properties of ($CoFe_2O_4$) hard ferrites show low value of saturation magnetization (Ms) for alkaline as a catalyst compared with used acid as a catalyst, which have a value of saturation magnetization (Ms) is high Up to 50 (emu/g).

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