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The effect of preparation method and presence of impurity on structural properties and morphology of iron oxide

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Abstract: In this paper, the effect of the structural properties and morphology of iron oxide product, have been studied in co-precipitation and hydrothermal methods. Also, the effect of adding CCl_4 impurities and final annealing of the materials is taken into account. The more homogeneous particle size in hydrothermal method has been explained by the effect of adding CCl_4 as impurities to prevent the continuation of nucleation. It has also been observed that in co-precipitation sample additive has a key role for providing the bar shape particles by mediating of the anisotropic connection of nuclei. The difference in the crystal structure of the anneal samples has been related to the oxygen content.

Keywords: Iron oxide, Co-precipitation, Hydrothermal, CCl_4 Additive, Bar structure shape.

1. Introduction

Metal oxides play an important role in chemistry, physics, and materials science. Now a days, magnetic nanoparticles, magnetite, are of particular vital scientifically and technologically.

Fe_3O_4 nanoparticles were used in biomedical, agriculture, industry, and data storage [1, 2]. In these applications, magnetic, catalytic, optical, and chemical properties of nanoparticles is strongly dependent on the particle size, particle shape, structural features, impurities and stoichiometry [3, 4].There have been many attempts to control these parameters, one of the ways were used to control

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the properties of iron oxide nanoparticles is the modifying of manufacturing method [4].

The other way to control the properties of iron oxide nanoparticles is the usage of different additives as raw materials to affect the velocity of growth or nucleation mechanism that can change the results of the manufacturing process [2]. In addition, it is possible that impurities enter to lattice structure and affect other properties. For example, addition of Ag and Au impurities, led to nanoparticles with nanowires and dumbbell shape respectively [5, 6]. A suggestion is the usage of carbon tetrachloride (CCl_4) as additive. CCl_4 is one of the chlorides compounds like the other raw material ($FeCl_3$ and $FeCl_2$) used in this project and also has a symmetrical molecule shape. The carbon atoms have a smaller diameter than iron and the presence of these atoms increase the possibility of occurrence of lattice displacement. It releases that presence of extra Cl^- ions can have a great impact on the reaction kinetics. Therefore, in this study the effect of CCl_4 on the structural characteristics and morphology were also investigated.

2. Materials and methods

Iron oxide nanoparticles were prepared by co-precipitation method. For this purpose $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ with the molar ratio of 2:1 was added to distilled water and was stirred for half an hour using a magnetic stirrer at the temperature of approximately 60 ^oC. Then 30mL of NH_3 was dropped to mixture to form Fe_3O_4 phase. Magnetic particles was separated after three times washing with distilled water and finally dried; the sample was named as SR.

To study the effect of CCl_4 additive on nucleation and growth process, a series of samples were prepared by the same method; the only difference is the presence of CCl_4 with a same molar ratio of $FeCl_2.4H_2O$. The result was named SRC.

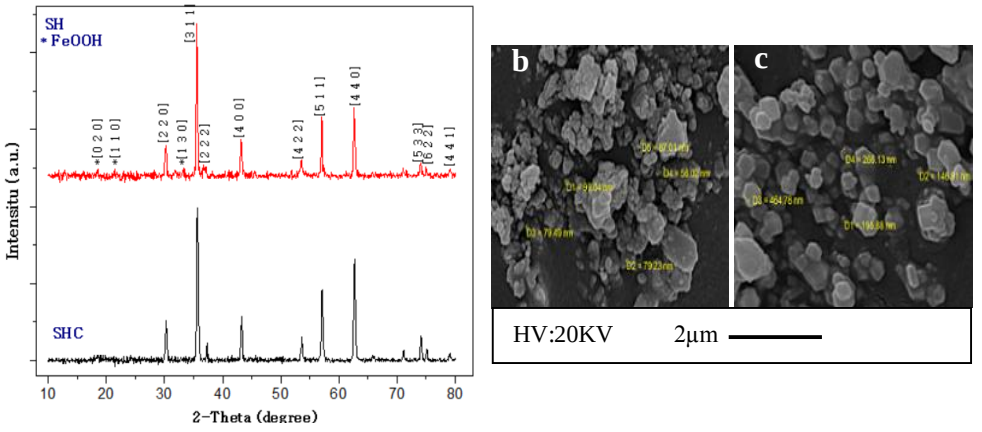
To study the effect of synthesis process, SH and SHC samples were prepared by hydrothermal method. The iron chloride ($FeCl_2.4H_2O$), sodium hydroxide (NaOH) and hydrazine hydrate ($N_2H_4.H_2O$) was used as the starting material. After adding the appropriate ratio [7] to distilled water, the solution is poured into an autoclave for 6 hours at 130 ^oC and ultimately resulting material was dried. The SRC and SHC samples were annealed for an hour at 300 ^oC to obtain SRC300 and SHC300 samples. The morphology of samples was studied using SEM images. XRD analysis was used to determine the structural characteristics of samples. Crystallite size of the samples was calculated using Scherer model.

3. Results and discussion

Comparison of the two hydrothermal samples SH and SHC:

Color of the SH and SHC sample were determined in black and dark brown respectively. Figure 1 (a-c) shows XRD and SEM analyses of these samples.

According to XRD and x'pert analyses, in SH sample cubic structure Fe_3O_4 phase was formed with a space group Fd-3m. Moreover, lattice parameter was 8.371 Å. This value is close to the value reported by Johnson et.al [8]. The presence of small additional peak indicates FeOOH impurities which resulted in brown color observed in this sample. In SHC testing, Fe_3O_4 phase is formed with similar structure and crystal symmetry to SH. The lattice parameter in this sample was 8.365Å which is slightly smaller than the SH sample that can be due to the changes in oxygen of composition, the possibility of carbon atoms existence in the structure or the difference between the ambient pressure in the process of phase formation. In particular, lattice parameter changes with changing the oxygen content is a known phenomenon. Also a change in the relative intensities of the peaks can be observed, which may be due to differences in lattice ordering of two samples.



Fid. 1. a) XRD analysis of SH & SHC SEM images b)SH c)SHC

According to Scherer equation the crystallite size of SH and SHC was about 70nm and 40nm respectively. As can be seen in SEM image the particle size of SH sample is less than 100 nm. However, in when the particles stick together some particles are created at the level of micron size and the shape f particles is spherical and symmetric. In SHC sample the size is in range of 200nm. The relative difference between the particle size of two samples are in agreement with the calculated crystallite size.

SHC sample is more homogeneous considering particle size and shape. The particles can be observed in rectangular and hexagonal shapes. In fact, by adding CCl_4, particle size gets more homogenous and the crystalline grains get larger. It seems that the presence of CCl_4 has strengthened the growth and prevented the continuation of the nucleation process to the final stages of production. The differences mentioned in the crystalline order in the previous section can be attributed to the difference in growth rates of the two samples.

Comparison of the co-precipitation samples (SR) and (SRC):

The XRD and SEM images of both black powders samples is shown in Figures 2 (a-c).

According to x'pert analysis the SR sample is Fe_3O_4 phase with cubic structure. Its space group is Fd-3m and the lattice parameter is equal to 8.305Å. Since the sample is made exposed to the air, there was no limitation to absorb oxygen and the smaller lattice parameter of this sample against those made by hydrothermal method can be attributed to higher oxygen content in the sample. SRC sample consists of two phases, the predominant phase (about 75%) is Fe_3O_4 compound and its structure is similar to the previous samples except that the lattice parameter in this case is much smaller and equal to 8.116Å. The second phase of this sample corresponds of the solid composition of NH_4Cl. Small shifts in some of the peaks of the Fe_3O_4 in the sample is indicative of distortion in the crystal structure. This distortion has a close relation with anisotropic growth and bar structures shown in the SEM image. The crystallite size of SR and SRC is 10 nm and 12 nm respectively. Therefore, we can conclude that the growth process in SRC was a few stronger than the SR while the nucleation process was more active in SR sample. In fact, the presence of CCl_4 can create the conditions need for welding of the crystalline grains and the formation of bar shape polycrystalline structure.

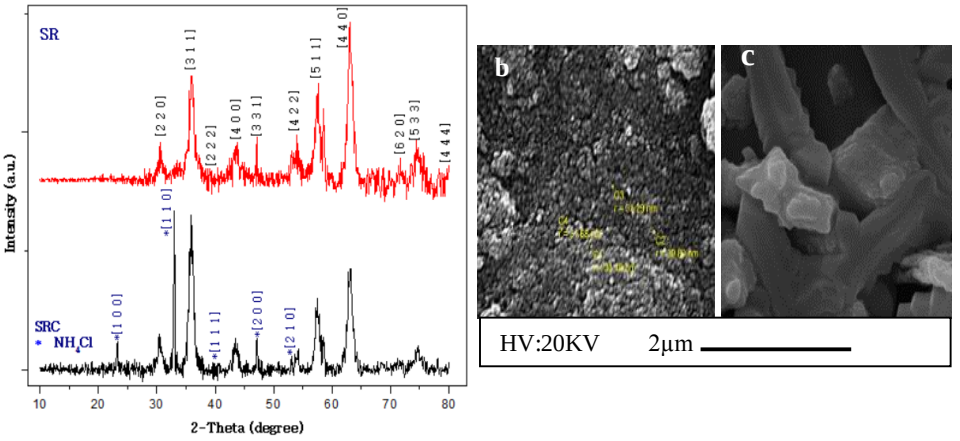


Fig. 2. a) XRD analysis of SR & SRC SEM images b)SR c)SRC

According to SEM image the shape of grains in SR sample is spherical and symmetric and their average size is about 23nm. However, it can observed that in SRC sample the presence of CCl_4 result in the formation of bar shape particles with a few microns length and the diameter of around 700nm.

Effects of Annealing:

Two SRC300 and SHC300 samples was obtained by annealing of SRC and SHC samples at 300°C, XRD and SEM images is shown in Figure 3 (a-c). Both samples are dark red powders. According to XRD analysis shown in Figure 3(a) the SHC300 sample is

γ-Fe_2O_3 with space group of Fd-3m and cubic structure and the lattice parameter is 8.321 Å. Also a distortion is observed in the structure.

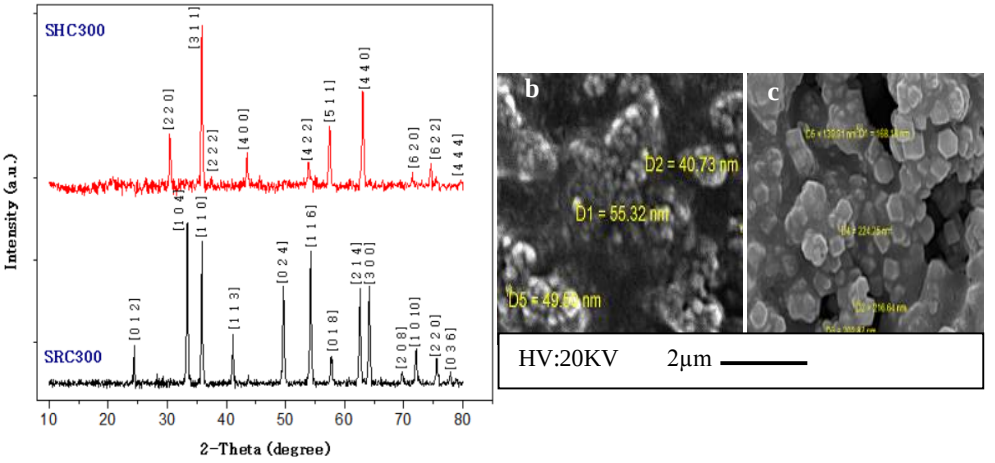


Fig. 3. a) XRD analysis of annealed SEM images of the annealed b) SHC300 c)SRC300

NH_4Cl impurities in the SRC sample has been removed during annealing, also a new phase is formed compare to previous samples. The composed phase is Fe_2O_3 with rhombohedral structure with the space group of R-3c. The lattice parameters are a=b=5.023 Å and c=13.73 Å, respectively. This value is close to the value reported by Minhoua and colleagues [9]. Oxidation of Fe_3O_4 into Fe_2O_3 particles is a known issue.

Since in hydrothermal method the experiments has been dune under a closed container (autoclave) the samples has lower content of oxygen in compare with co-precipitation samples. Annealing the sample at 300°C there is a possibility of oxygen uptake. Although this value of oxygen absorption change the lattice but it was not enough the extent that the crystal change to rhombohedral structure.

According to SEM images contrary to what is usual, in both SHC300 and SRC300 sample particle size has been reduced.
The particle size of the SHC sample that was about 200 nm reached 50 nm by annealing. It seems that structural contraction of the crystalline grains by entrance of oxygen atoms and creation of negative pressure inside the structure weakened the bond between the grains and this results in a porous and granular structure, this behavior is similar to crushing of super-chilled ice while floating in lukewarm water.
Also by annealing the SRC sample at 300^{o}C bar shape structures removed and particles with regular shapes composed with the size of about 200 nm. Grain size obtained using Scherer formula for SHC300 and SRC 300 was 45nm and 35nm respectively.

4. Conclusion

For the synthesis of iron oxide two methods were used, including hydrothermal and co-precipitation. Comparing these two methods, co-precipitation sample has smaller particle size and is more homogeneous than the hydrothermal one. A small percentage of FeOOH composition made by hydrothermal method was observed and that's reason of brown color of the sample. Adding CCl_4 in co-precipitation method results in the presence of an impurity phase of NH_4Cl in the product. Also, by adding CCl_4, the bar shape structures were observed in dimensions of a few microns. The growth of particles in the hydrothermal sample was milder due to CCl_4 additive and in this method the presence of the additive has led to a product with more homogeneous particle size.
Annealing led to phase changing and creation of γ-Fe_2O_3 of cubic structure in the SHC300 sample and Fe_2O_3 with orthorhombic structure in SRC300. The Annealing of the samples at the temperature of 300^{o}C has led to the deflection due to internal contraction, and shrinking the size of particles in both samples and the elimination of NH_4Cl impurities in SRC300 sample.

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