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# Mechanochemical Synthesis of $Fe_2O_3$ Nanoparticles

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**Abstract**

In this work, formation of iron oxide nanoparticles by mechanochemical reactions in different milling times was studied. During the mechanical milling, the solid-state displacement reaction of $3Na_2CO_3 + 2FeCl_3.6H_2O = 6NaCl + Fe_2O_3.6H_2O + 3CO_2$ was induced to form iron oxide nanoparticles. A simple washing process was done to remove NaCl by-product and subsequently the particles dried at 105˚C for 12h. Nanoparticles size and the mechanochemical effect were characterized by X-ray diffraction (XRD) and particle size analysis. Experimental results show that increasing the milling time can effectively reduce the nanoparticle size of $Fe_2O_3$. The average $Fe_2O_3$ nanoparticles size is about 14 nm for 2h and 4 nm for 5h milling process.



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*Keywords:* Iron oxide ($Fe_2O_3$); X-ray technique; Nanoparticles; Mechanochemical.

## 1. Introduction

Nano-size particles of less than 100 nm in diameter are currently attracting more attention for the wide range of new application in many fields and industries because of some effects like small particle dimension, high surface to volume ratio and quantum confinement, Baláž et al. (2003), Li et al. (2005), Lu et al. (2008), McCormick et al. (2001), Pathak et al. (2012), Sabri et al. (2012), Tsuzuki and McCormick (2004). Mechanochemical processing is a new method involving the mechanical activation of solid-state chemical reactions displacement during ball milling which has been widely researched in the recent years and were used to synthesize of metallic, oxide and sulfide nanoparticles, Baláž et al. (2003), Li et al. (2005), Lu et al. (2008), McCormick et al. (2001), Shi et al. (2000), Tsuzuki and McCormick (2000), Yang et al. (2004), Yang et al. (2004). The other competitor methods that have

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been developed to synthesize nanoparticles include: sol-gel, vapor phase condensation, sputtering, wet chemical precipitation and hydrothermal synthesis. The main advantage of mechanochemical synthesis is that in this method the process carried out in solid state and agglomeration did not occur in comparison to the above methods. In addition, the control of the overall particle size distribution in this method is easier, Tsuzuki and McCormick (2004), Yang et al. (2004). During milling fracture, deformation and welding of the reactants take place. Chemical reactions occur at the interface of reactants, consequently the chemical reactions that require high temperature will occur at low temperature without any external applied heat, Baláž et al. (2003), Koch (1993). Mechanochemical synthesis was done by displacement reaction according to the following reaction:

$$A_xC + yB = xA + B_yC \quad (1)$$

where $A_xC$ and B are the reactants, A is favorable product and $B_yC$ is by-product of the reaction. By choosing suitable conditions such as milling parameters, suitable BPR and the stoichiometric ratio of starting materials, mechanochemical processing can be used to synthesize nanocrystalline particles. After the milling process, the nanoparticles will be surrounded with by-product materials which are dispersed within this soluble salt matrix, selective removal of the matrix phase must be done by washing the resulting powder with appropriate solvents. After that nanoparticles will be formed as small as 5 nm, McCormick et al. (2001), Tsuzuki and McCormick (2004). Nowadays fabrication of iron oxide nanoparticles has attracted a lot of attention due to their unique properties and industrial capability. In this research an investigation has been carried out to synthesize iron oxide ($Fe_2O_3$) nanoparticles by mechanochemical solid-state reaction between sodium carbonate ($Na_2CO_3$) and iron chloride hexahydrated ($FeCl_3.6H_2O$).

**Nomenclature**

BPR ball to powder weight ratio

## 2. Experimental

The chemical reagents, sodium carbonate (99%) and iron chloride hexahydrated (98.99%) were used as the starting materials for mechanical milling. These materials were mixed in stoichiometric ratio (3.69 gr of $Na_2CO_3$ and 5.45 gr of $FeCl_3.6H_2O$). The total weight of this mixture was 9.14 gr. The process carried out with a planetary ball-mill at room temperature, using BPR of 35:1. The starting materials were mixed and milled for 2 h and 5 h. Removal of the NaCl by-product was conducted by washing the powder with distilled water and drying at 105 ˚C for 12 h in the oven to remove water and obtain the nanoparticle precursor. After that the weight of the powder was measured carefully and the dried powder then subjected to XRD and particle size analysis. Structures of mechanically milled powders were examined using Philips X'pert PW 3040/60 X-ray diffractometer (XRD) with CuKα radiation and the particle size was determined using Vasco3 particle size analyzer.

## 3. Results and discussion

The flow chart of the mechanochemical synthesis process is given in fig. 1. The simple procedure of the nanoparticles formation (the milling step) and their separation and cleaning (the washing and drying steps) form the whole mechanochemical process of the iron oxide nanoparticles generation.

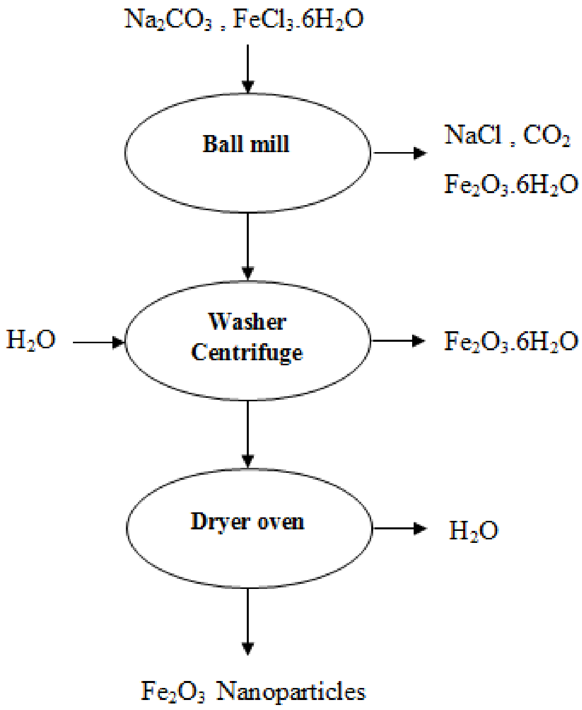


Fig. 1. Flow chart of mechanochemical synthesis of $Fe_2O_3$ nanoparticles.

Figure 2 shows the XRD pattern of the solid products after the mechanochemical reaction of $Na_2CO_3$ and $FeCl_3.6H_2O$ that were milled for 2 h and 5 h. The following reaction possibly occurs and NaCl was produced as a by-product:

$$3\ Na_2CO_3+2FeCl_3.6H_2O = 6NaCl + Fe_2O_3.6H_2O + 3CO_2 \quad (2)$$

After milling the powder mixture for 2 h and 5 h, it was observed that the XRD pattern is like an amorphous pattern and it could be said that the product is nanocrystalline sized iron oxide particles. The peaks of $Fe_2O_3.6H_2O$ and $Fe_2O_3$ with no NaCl phases are shown in fig. 2, indicating that the complete removal of the NaCl by-product phase was done by post-washing and final product is $Fe_2O_3$ nanocrystalline particles. It is obvious that the diffraction patterns of two specimens are similar, which indicates the formation of iron oxide ($Fe_2O_3$). The XRD patterns of the samples show broad peaks, which clearly indicates that the samples are nanocrystalline. The difference of the patterns is just in the broadening of the peaks. Broader peak indicates smaller crystallite size. From the graph, it is observed that the 5 h ball-milled sample crystallite size is smaller than 2 h ball-milled sample. Therefore, by increasing milling time the nanocrystalline particles with smaller size can be synthesized. Another feature which can be seen during milling is that the colour of the final mixture changed frequently and at last remained red. This colour can be another sign that the produced particles must be iron oxide.

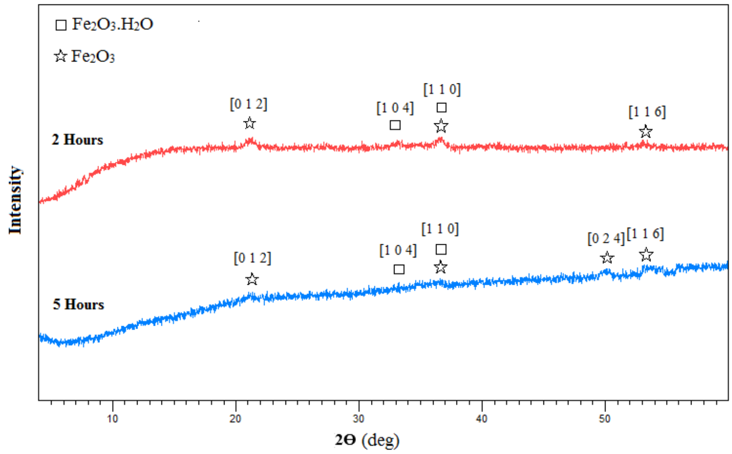


Fig. 2. XRD patterns of $Na_2CO_3 + 2FeCl_3.6H_2O$ powder mixture after milling for 2 h and 5 h.

In order to estimate the size of $Fe_2O_3$ nanoparticles the particle size analysis was applied and the average particles size was calculated by Cumulant method. For this analysis due to agglomerated product of the milling process, at first the product was abraded in Agut pounder and then 20 cc of ethanol was added. Afterwards the powder was dispersed in glycerol dispersion solution for 2 h and after good dispersion, particle size analysis was done. The plots of the particles volume fraction versus particle size for the sample with 2 h milling time and 5 h milling are shown in fig. 3, respectively.

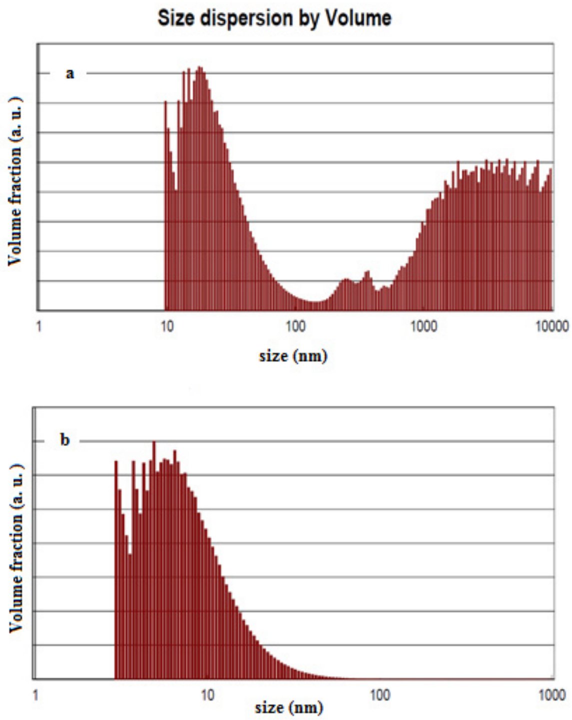


Fig. 3. Volume fraction against $Fe_2O_3$ particles size. (a) for 2 h ball-milled sample; (b) for 5 h ball-milled sample.

Table 1 shows the results of the particle size characterization which have performed in the glycerol disperse solutions. Table 1 shows that increasing the milling time can be led to smaller nanoparticles and the sample with 5 h milling time has smaller size than the sample with 2 h milling time.

Table 1. The average nanoparticles size, extracted from particles size analysis, dispersed for 2h using glycerol as dispersant solution.

| **Sample** | 2 h milling | 5 h milling |
|---|---|---|
| **Dispersant** | Glycerol | Glycerol |
| **Average particle size (nm)** | 14.01 | 4.21 |

## 4. Conclusion

In the present work, formation of nanoparticles by mechanochemical processing of $Na_2CO_3$ with $FeCl_3.6H_2O$ has been studied. This work was resulted in the formation of amorphous precursor during milling, which was then oxidized to nanocrystalline $Fe_2O_3$ after thermal treatment at 105 ˚C in oven. The XRD pattern shows the presence of $Fe_2O_3$ in the final product. Particle size analysis determined that the size of the $Fe_2O_3$ nanoparticle decreased with increase in milling time from 2 h to 5 h. The average nanocrystalline particles size was about 14 nm for 2 h ball-milled sample and 4 nm for 5 h ball-milled sample.

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