

Short Communication

Investigation on Influences of Synthesis Methods on the Magnetic Properties of Trimetallic Nanoparticles of Iron-Cobalt-Manganese Supported by Magnesium Oxide

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Abstract

Using $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ the magnetic properties of nanoparticles trimetallic Iron - Cobalt - Manganese, with supported Magnesium oxide have been prepared by Co-precipitation and Solvothermal methods. The prepared samples are characterized by Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Vibrating Sample Magnetometer (VSM) and Brunauer-Emmett-Teller (BET) surface area measurements. Data from SEM showed spherical and nearly uniform spherical shape particles for the samples which were synthesized with support by co-precipitation and by solvothermal methods, respectively. According to the patterns of XRD, the crystal size of the nanoparticles prepared by co-precipitation method with support are in the range of 25 to 30 nm and the size of the particles are in the range of 45 to 50 nm using solvothermal method. The results of the BET from all of the nanoparticles synthesized show that precursors have highest surface area of the calcinated samples. According to the VSM results taken at room temperature (RT), the samples with support after calcination were placed in the category of soft ferromagnetism.

Keywords: Catalyst, Co-precipitation, Nanoparticles, Soft ferromagnetism, Solvothermal.

1. INTRODUCTION

In recent years, Nano science and Nano technology, have become especially to a branch of special research with specific applications [1]. The properties and applications of nanoparticles are subjects that have been much researched about them because they have unique physical and chemical properties [2, 3]. The magnetic properties of materials in Nano-scale are used in high-density recording, image color, high-frequency devices and so on [4]. Nanoparticles of tri-metallic alloys have especially applications in the petrochemical and synthetic fuels. Synthetic fuel and Fischer-Tropsch reaction are important issues for scientific research with economical advantage in the twenty-first century. In general, Fischer-

Tropsch reaction includes CO hydrogenation on heterogeneous catalysts which is an economical process to convert synthesis gas (a mixture of Hydrogen and Carbon monoxide) to a wide range of Hydrocarbon products. Although, several metals have been known as catalysts for this reaction but the Fischer-Tropsch reactions of synthesis have industrial and commercial aspects only on catalysts based on Iron and Cobalt. Amongst the transition metals [5-6], the most common metals as a catalyst in the synthesis Fischer-Tropsch are VIII metals such as Rh, Ru, Ni, Co, Fe [7].

The synthesis of trimetallic nanoparticles represents an emerging strategy to maximize catalytic performances in noble

metal-based catalysts. However, the controllable synthesis of trimetallic nanomaterials as well as the exact role played by the addition of a third metal in their composition over catalytic performances remains unclear. Trimetallic nanoparticles have shown improved catalytic

performances relative to their mono- and bimetallic counterparts for a variety of reactions that include Cyclohexene and Glucose oxidation, the electro oxidation of formic acid, and C-C coupling [8-10]. Despite these very attractive features, studies on the synthesis of trimetallic noble metal nanomaterials are still limited, and the role of the third metal over the performances, relative to their bimetallic systems, remains unclear [11]. Trimetallic nanoparticles may possess an even greater degree of catalytic activity and selectivity than the bimetallic ones because more variables (such as tuning) are available, however, there have been only a few report of trimetallic nanoparticles in literatures thus far [12-13]. Selection a method of syntheses of Nano-particles is very important and depends on the chemical composition, application, and laboratory facilities, economic cost, type of initial reaction and so on, which should be considered when selecting a method of making Nano-materials. In general, the methods of making Nano materials are divided into three categories:

1- Physical methods 2- Chemical methods
3- Mechanical methods [7]. The purpose of this study is investigation of influence of synthesis methods, such as co-precipitation and solvothermal methods, on the magnetic properties of the Iron, Cobalt, and Manganese nanoparticles by adding support of Magnesium Oxide.

2. PREPARATION PROCEDURES

2.1 Preparation of the samples by co-precipitation method

In the co-precipitation method for preparing nanoparticles of metallic Iron, Cobalt, Manganese, were prepared two

molar solution of nitrate salts $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 M) (99% Merck), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2 M) (99% Merck) and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2 M) (99% Merck) with the same molar ratios were premixed and then the 10 wt.% of MgO (based on the total catalyst weight) was added to mixed solution of Cobalt, Iron and Manganese Nitrates. The resulting solution was heated to 70°C in a round bottom flask fitted with a condenser. Aqueous Na_2CO_3 (2 M) (99% Merck) was added drop wise to the mixed nitrate solution with stirring while the temperature was maintained at 70°C until $\text{pH} = 9.7 \pm 0.1$ was achieved. The resulting precipitate was then left in this medium for 2 hrs. The aged suspension was filtered and then washed several times with warm distilled water until no further Na^+ was observed in the washings [12], as tested by flame atomic adsorption. The precipitate material was then dried in an oven at 120°C for 12 hrs to get a material denoted as the catalyst precursor, which was subsequently calcinated in static air in a furnace at 600 °C for 6 hrs.

2.2 Preparation of the samples by solvothermal method

In this study, also the supported Iron-Cobalt-Manganese was prepared using solvothermal synthesis. At first 31.4 ml Toluene and 5.11 ml Oleylamine were mixed [13]. Then, 2.56 gr of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2 gr of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 2.24 gr of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to the solution and 0.68 gr MgO was added as support to the mixed solution. The resulting solution was stirred for 1 hr until became quite uniform. Consequently, the solution leaved in a 50 ml Teflon-Lined stainless steel autoclave, after that the autoclave was allowed to heat up to 180°C for 18 hrs. In the next step the autoclave remained in off oven condition for 2 hrs and after that autoclave naturally cooled to room temperature. The precipitate was separated by centrifugation and has been washed with Ethanol in two times. Finally the products have been calcinated at 600°C

for 6 hrs and the sample has been powdered in mortar.

3. RESULTS and DISCUSSIONS

3.1 Results of Scanning Electron Microscope

The shape and size of the sample were determined using SEM system, model MIRA II LMU/TESCAN located in the Iranian Research Organization for Science and Technology. Figures 1 and 2 show SEM images of trimetallic nanoparticles with the support MgO prepared by co-precipitation method before and after calcination respectively. In the Figure 1, the pre-calcinated particles have stucked together, but after calcination (Figure 2), most of particles have became nearly spherical and average size of particles were about 30 nm (using ruler and MATLAB softwares).

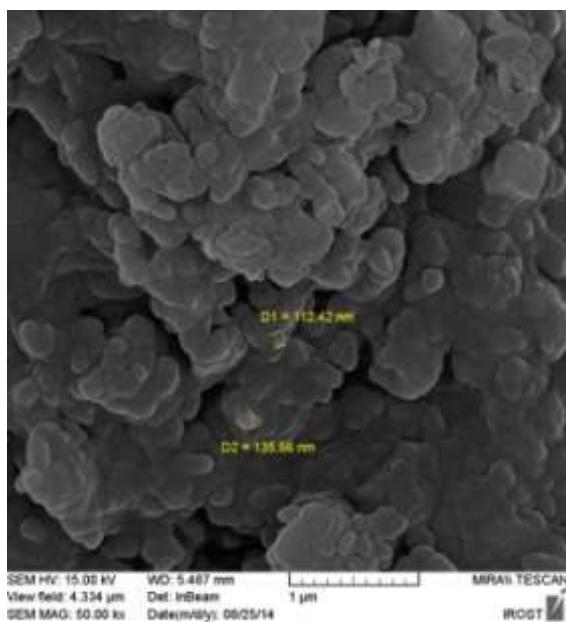


Figure1: SEM image of nanoparticles prepared by co-precipitation with MgO support before calcination.

Figures 3 and 4 show nanoparticles that produced by solvothermal, which represent better uniformity. In this method, we can see from Figure 3 that the particles have been stucked together before calcination, but after calcination (Figure 4), most of the particles have been found uniformly and

spherical in average size 45 nm. So, we can say that the changing method could affect size and distribution of nanoparticles.

The results of the SEM images show that the produced samples by co-precipitation method are more agglomerated nanoparticles respect to the ones which produced by solvothermal method.

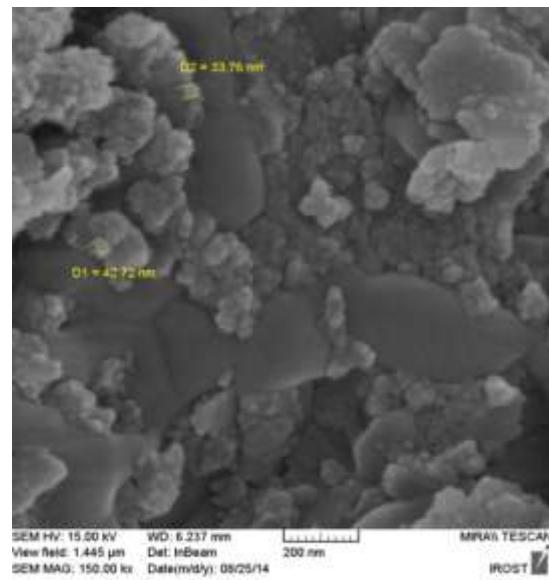


Figure2: SEM image of nanoparticles prepared by co-precipitation with MgO after calcination.

Using solvothermal method is available to achieve better nanoparticles with spherical morphology and particle size distribution. It should be noted that other important factors can show effects on the performance of the nanoparticles such as phases in the sample, the distribution of particles in the tissue sample and the sample structure.

3.2 Results of X-Ray Diffraction

To determine the crystalline phases of the samples, a XRD X-TERT model manufactured by PHILIPS in Tehran University has been used. Anode is copper tubes with wavelength 1.54056 \AA , voltage 40 kV and current 30 mA. Figure 5 shows results of X-ray diffraction and Table 1 shows crystalline phases and peaks

intensity of the samples that prepared by co-precipitation method.

Table1: Results of XRD for the samples that produced by co-precipitation method

Peak No	Crystalline Phases	20
1	CoMnO ₄	15.78
2	Fe ₂ O ₃	35.60
3	CoMnO ₄	38.31
4	C ₃ N ₄	45.80
5	CoFe ₂ O ₄	62.81
6	CoFe ₂ O ₄	66.09

The average size of the particles is 27 nm and a maximum intensity is observed at an angle of 35.60°. The MgO supported samples that prepared by co-precipitation method have phases such as: Fe₂O₃ (Rhombohedral), CoFe₂O₄ (cubic), CoMnO₃ (Cubic).

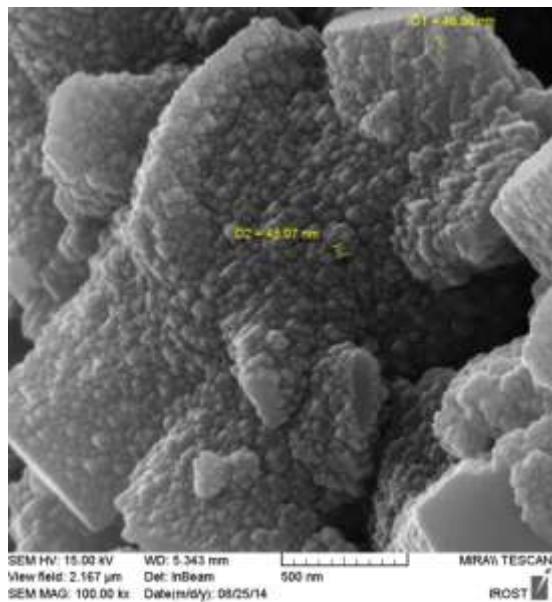


Figure3: SEM image of nanoparticles prepared by solvothermal with MgO support before calcination.

Table2 shows crystal phases and the intensities of peak points from the XRD spectra of the samples that prepared by solvothermal method. The average particle

size is 47 nm and a maximum intensity is observed at an angle of 35.54°. Also Table 2 shows that the sample prepared in this method, involves MgFe₂O₄ (Cubic) and Fe₂O₃ (Rhombohedral) Phases. Figure 6 shows XRD spectrum of the trimetallic Iron-Cobalt-Manganese supported MgO prepared by solvothermal.

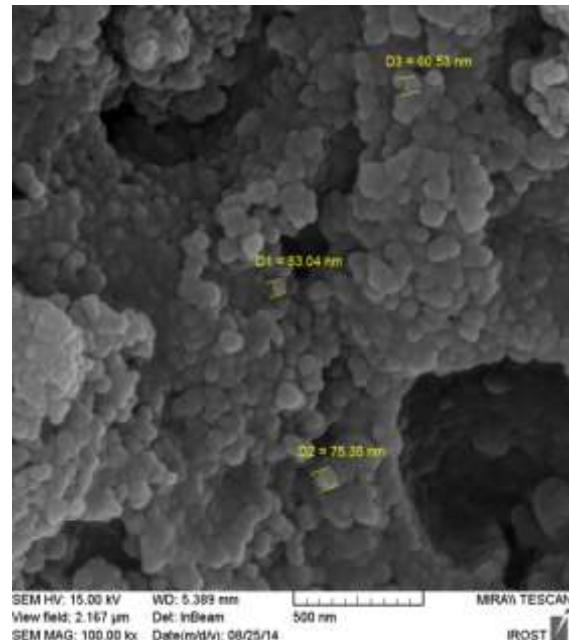


Figure4: SEM image of nanoparticles prepared by solvothermal with MgO support after calcination.

3.3 Results of BET

To measure the specific surface area, BET device was used (Quanta chrome TPR Win v1.0 model at the University of Sistan and Baluchestan, I.R.Iran). In all nanoparticles, precursor has the highest surface area than the calcinated samples. After calcination, in all cases there are reductions in the surface area compared to the precursor. This is because in the sample of precursor crystalline, water is absorbed; the loss of waters during the BET measurements produces vacuolation on the surface that cause an increase in the surface area. In the calcinated sample, the water in the sample is absorbed. The waters, crystallization, are removed during calcination. Consequently it has surface area smaller than precursor. The surfactant

increases surface area and decreases size of particles that prepared by solvothermal. It can be said, because the MgO support with Oleylamine as reductive factor was used in solvothermal method, causes an increase in concentration and reduces the volume of solvent in autoclave and resulting in decreased surface area respect to co-precipitation method.

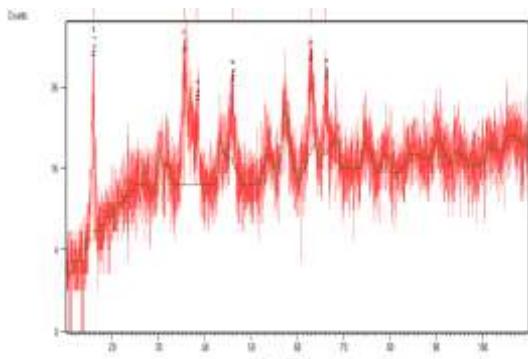


Figure 5: XRD spectrum of the trimetallic Iron-Cobalt-Manganese with MgO prepared by co-precipitation.

Table2: Results of XRD for the samples produced by solvothermal method

Peak No	Crystalline Phases	2θ
1	MgFe ₂ O ₄	18.38
2	Fe ₂ O ₃	30.14
3	MgFe ₂ O ₄	35.54
4	Fe ₂ O ₃	43.22
5	MgFe ₂ O ₄	53.62
6	MgFe ₂ O ₄	57.16
7	Fe ₂ O ₃	62.74
8	MgFe ₂ O ₄	74.31
9	MgFe ₂ O ₄	79.33
10	Fe ₂ O ₃	87.13
11	MgFe ₂ O ₄	89.96

4.3 Results of VSM

All of magnetic measurements have been done by VSM system where is located in the Nano Magnetic Laboratory, in the University of Sistan and Baluchestan, Zahedan, Iran, The system is made of

Meghnatis Daghighé Kavir, (MDK), Company, Kashan I. R. Iran [14]. Figure 7 shows magnetization curve in terms of the intensity of the magnetic field for the samples of trimetallic with Magnesium oxide support that have prepared by co-precipitation method before calcination. The sample has a saturation magnetization 0.65104 emu/gr and residual magnetization 0.01353 emu/gr and the coercivity of 100 Oe. Because the coercivity is 100 Oe, so this material is ferromagnetic, and has not reached to the saturation level.

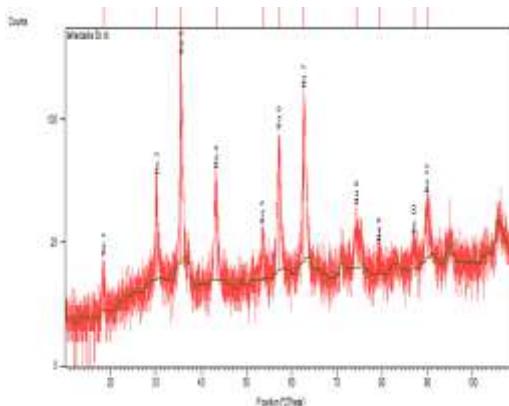


Figure6: XRD spectrum of the trimetallic Iron-Cobalt-Manganese supported MgO prepared by solvothermal.

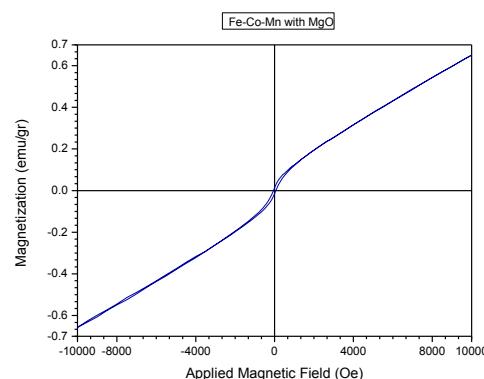


Figure7: Curve of M-H for the sample of trimetallic Fe-Co-Mn with MgO support before calcination prepared by co-precipitation.

The graph in the Figure 7 can be divided into two parts: 1. field between -2000 to +2000 Oe with ferromagnetic properties, and coercivity of ± 100 Oe for the sample,

2. field from ± 2000 to ± 10000 Oe where the sample has not saturated.

Figure 8 shows magnetization curve in terms of applied external magnetic field for trimetallic sample with magnesium oxide support which is prepared by co-precipitation method after calcination. The sample has a saturation magnetization of 6.09519 emu/gr and residual magnetization of 0.31191 emu/gr. If we have a look at the range between -4000 to $+4000$ Oe according to the area under the curve, hysteresis loop is very low, so it can be said that the sample is in soft ferromagnetic materials' category.

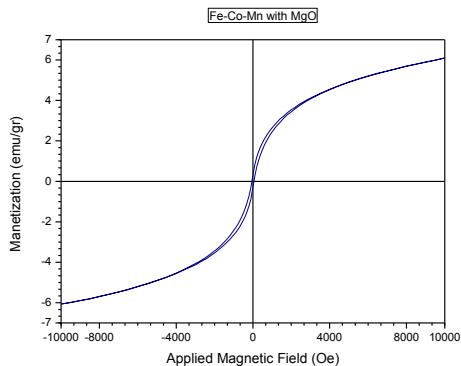


Figure8: *M-H curve for the trimetallic Iron-Cobalt-Manganese with MgO support after calcination prepared by co-precipitation.*

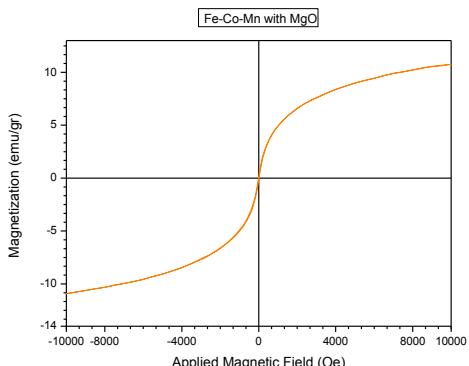


Figure9: *Curve of M-H for the sample of trimetallic Iron-Cobalt-Manganese with MgO support before calcination that prepared by solvothermal.*

Figure 9 shows magnetization curve in terms of the external applied magnetic field for the sample of trimetallic with

magnesium oxide support that is prepared by solvothermal method before calcination. The sample has a saturation magnetization of 10.7545 emu/gr and residual magnetization of 0.1511 emu/gr and the coercivity of zero Oe. We can consider the sample as superparamagnetic since the coercivity is zero, and because of the phases of production, Fe_3O_4 and Fe_2O_3 pre-calculated.

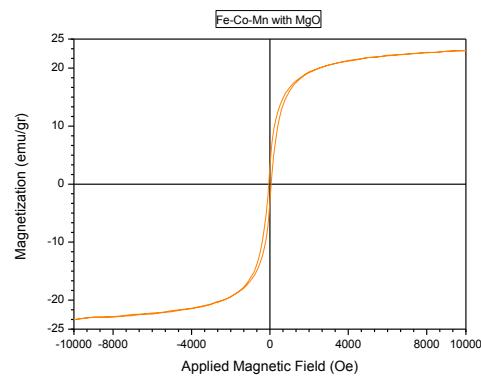


Figure10: *curve of M-H for the trimetallic Iron-Cobalt-Manganese with MgO support after calcination that prepared by solvothermal.*

Figure 10 shows magnetization curve in terms of magnetic field for the sample of trimetallic with magnesium oxide support that is prepared by solvothermal method after calcination. The sample has a saturation magnetization of 6.09519 emu/gr and residual magnetization of 0.31191 emu/gr and the coercivity of 100 Oe and according to the information obtained from this curve, it is placed in the category of ferromagnetism.

For the above sample, when we put the sample into the oven at 600°C , for the smaller size particles, occur more easily that the direction of the magnetic moments to be aligned. So, magnetization is related to particle size, and in a certain field, the smaller particles will be more magnetized. According to phases in the spectrum of XRD, Fe_2O_3 and MgFe_2O_4 compounds have different magnetic properties. By substitutions of ions of magnesium with magnetic Iron in both the octahedral and

tetrahedral states, it may change the interaction and exchange in the two situation. Therefore it creates different effects on the magnetic properties of the sample. Several experimental studies of the relations between coercivity and particle size have been reported [15-18].

4. CONCLUSION

In this study, trimetallic nanoparticles, Iron – Cobalt, Manganese, with supported Magnesium oxide have been prepared by co-precipitation and solvothermal methods. The prepared samples are characterized by Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Brunaer-Emmett-Teller (BET) surface area measurements and Vibrating Sample Magnetometer (VSM). The results of SEM images showed that the particles were spherical in co-precipitation method with MgO as support. However, in solvothermal method, the synthesized samples had distribution and uniformity better than co-precipitation method and they were almost spherical. The XRD results showed that in co-precipitation

method, particle sizes were between 25 and 30 nm and in solvothermal method, particle sizes of approximately were 45 to 50 nm. The results of VSM at room temperature show that, the sample which was prepared by co-precipitation with MgO support, pre-calcined had diamagnetic properties, but after calcination at 600°C and the removal of some phase, it became soft ferromagnetic. Moreover, the sample that was prepared with MgO support after calcination at the same temperature, because of having small area under the curve, it is categorized as soft ferromagnetic materials.

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