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Short Communication

Characterization of Cobalt Oxide Co_3O_4 Nanoparticles Prepared by Various Methods: Effect of Calcination Temperatures on Size, Dimension and Catalytic Decomposition of Hydrogen Peroxide

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Abstract:
In this scientific research work we report a novel method to synthesis Co_3O_4 nanoparticles via calcinations of cobalt hydroxide which can be conveniently prepared by the $Co(NO_3)_2.6H_2O$ with different reactants. In order to study the effect of calcination temperature on structure and morphology of the nanoparticles, the calcinations take place at various temperatures (at 300°C, 500°C and 700°C). The nature of cobalt oxide species depending on heat treatment. The samples at low temperature show decrease on size and dimension. The characteristics of the nanoparticles were investigated by XRD patterns, IR spectroscopy and scanning electron microscopy (SEM). It indicates that at higher temperature, greater nanoparticles were produced. Decomposition of H_2O_2 showed that calcination at 300°C result to higher activity.
Keywords: *Cobalt oxide, Microemulsions, Nanoparticles, Hydrogen peroxide, Calcination temperatures.*

1. INTRODUCTION

Transition metal oxide have many applications of interesting properties arising due to their variable oxidation state [1]. Cobalt oxide Co_3O_4 is an important transition metal oxide because of its application in various field of research and industry include pigments, gas sensor, magnetic materials, catalyst, anode materials for rechargeable Li-batteries, electrochromic devices, electrochemical systems and high-temperature solar selective absorbers [2-12].

The difference in oxygen defect, oxygen holes and oxygen adsorbed in different state of cobalt in Co_3O_4 (a mixed valance material that is formally $Co^{II} Co^{III} O_4$) [13] are thought to be the reason for high activity and selectivity of this metal oxide catalysts [12].

Therefore, in this field a variety of methods have been reported for preparing Co_3O_4 such as the thermal decomposition of cobalt precursors under oxidizing condition (210-815°***C***) [7, 14-19], chemical spray pyrolysis (300-400°***C***) [4, 20-23], chemical vapor deposition (CVD) [24], sol-gel [25, 26], microemulsion [1, 16], solvo thermal [27], hard templating [14], hydrothermal [3, 11], mechanochemical [2] and chemical combustion [28]. Nevertheless, all of the above physical and chemical methods need some special instruments and harsh conditions. In this paper we report

different methods and procedures with their morphology, discouse their X-Ray pattern and IR spectra. However to the best of our knowledge, there has been no report on the preparation of spinel-type Co_3O_4 nanoparticles via cobalt hydroxide obtained from cobalt nitrate and potassium hydroxide in aqueous media and from reverse micellar method with PVP as surfactant. However we report a novel precipitation method that is more facile, easy, simple and effective to synthesis Co_3O_4 nanoparticles that have not been reported in the literatures.

2. EXPERIMENTAL

2.1. Synthesis (Sample preparation)

In the method I cobalt nitrate $Co(NO_3)_2.6H_2O$ (0.6 M) was dissolved in 100 ml. deionized water. Then 100 ml. KOH aqueous solutions (3.2 M) were added drop wise to the precursor solution. Pink precipitate appeared immediately which easily to oxidized by air and low heat or weak oxidizing agents to $Co(OH)_3$. The dark brown precipitate was separated and washed with deionized water and dried in an oven at 110°C for 20 hours. The dried cobalt hydroxide was ground and preserved in a desicator.

$$Co(NO_3)_2.6H_2O + KOH \longrightarrow Co(OH)NO_3 + KNO_3$$
$$Co(OH)NO_3 + KOH \longrightarrow Co(OH)_2 + KNO_3$$
$$4\,Co(OH)_2 + O_2 + H_2O \longrightarrow 4\,Co(OH)_3$$

For the preparation of cobaltic-cobaltous oxide Co_3O_4, the dark brown cobaltic hydroxide was heated at 300°C, 500°C and 700°C for 3-4 hours.
In the method II cobalt nitrate and cobalt (III) hydroxide separately were weighed (5gr.) and ground to a preferred size and then transferred into two different crucibles and exposed to microwave energy (600W) in a microwave oven for 20 minutes. At the end of the experiment, the samples were allowed to cool inside the oven. The microwave-assisted decomposition reaction of cobalt nitrate hexahydrate and cobalt (III) hydroxide represented as follow:

$$3Co(NO_3)_2.6H_2O \longrightarrow Co_3O_4\,(s) + 6NO_2\,(g)\uparrow + 18H_2O\,(g)\uparrow + O_2\,(g)\uparrow$$
$$6Co(OH)_3 \longrightarrow 2Co_3O_4\,(s) + 9H_2O\,(g)\uparrow + \tfrac{1}{2}\,O_2\,(g)\uparrow$$

During microwave radiation a decomposition reaction took place and caused NO_2 and O_2 gases to be released from the cobalt nitrate sample.
In the method III the synthesis of cobalt oxide utilized two microemulsions. Micro emulsion (a) composed of polyvinylpyrrolidone (PVP) as surfactant, n-butanol as the hydrocarbon phase, and 5% cobalt nitrate solution as the aqueous phase. Microemulsion (b) had the same constituents as microemulsion (a) except that the aqueous phase was a solution of ammonium nitrate (2.5%) instead of cobalt nitrate. The weight fractions of various constituents in these microemulsions were as follows:
19% of PVP, 13% of the aqueous phase and 68% of n-butanol [1]. These two microemulsions were mixed slowly and stirred for 5 hours on a magnetic stirrer. The resulting precipitate was separated from the polar solvent and surfactant by centrifugation with 8000 rpm/min in 30 minutes. The precipitate washed for several times and was dried in air and then heated at 300°C for 24 hours to obtain cobalt oxide Co_3O_4 nanoparticles.

2.2. Catalytic decomposition of Co_3O_4 calcined at different temperature

H_2O_2 undergoes an exothermic reaction to form O_2 and H_2O. ($H_2O_2 \rightarrow H_2O + O_2$)
In this paper, the decomposition of hydrogen peroxide, was studied with catalyst Co_3O_4 with concentration of 5% at room temperature. Catalytic measurements were carried out by using the gasometric technique about 0.1g of the catalyst was added to a known amount of hydrogen peroxide (10 ml, 5%v/v) taken in a closed reaction vessel and the contents were stirred at 313 K. The volume of oxygen evolved was measured at regular time intervals.

2.3. Charactrization

X-ray powder diffraction (XRD) were recorded using Scifert3003TT, X-ray diffractometer with high density Cu Kα radiation (λ=1.54°A). The IR-spectrometer was taken on Perkin-Elmer 783 with sample as KBr disc, FT-IR spectrum was taken on Perkin-Elmer Spectrum 100 and the scanning

electron microscopy (SEM) of samples were carried out on a TESCAN-VEG II electron microscope with an accelerating voltage of 15 KV.

3. RESULTS AND DISCUSSION

3.1. IR

IR spectra of cobalt (III) hydroxide obtained from method I showed in figure 1. There are three strong bands due to the υ(-OH) modes, at 3000-3500 cm^{-1} and 1600 cm^{-1} due to Co-ONO or H_2O, 1400 cm^{-1} due to the stretching modes of Co-ONO, 600 cm^{-1} due to the bending modes of Co-NO and 512 cm^{-1} due to the M-O.

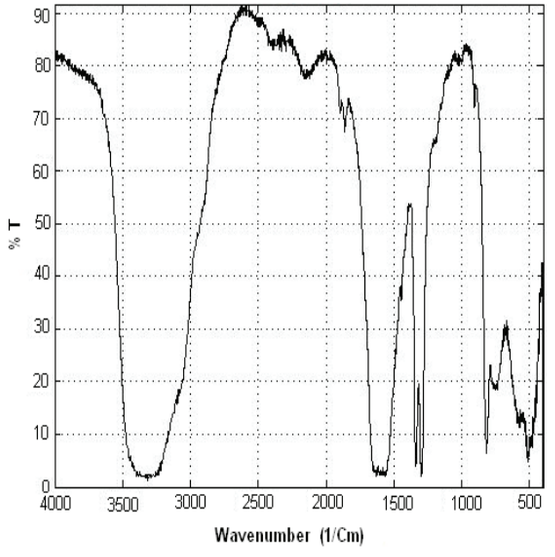

Figure 1: *IR spectra of cobalt hydroxide.*

In figure 2 showed IR spectra of tri cobalt tetra oxide (Co_3O_4) which obtained from calcinations of cobalt hydroxide (a, b) and cobalt nitrate (c). There are two strong bands due to υ(Co-O) modes at ~662cm^{-1} and ~576 cm^{-1} in figure 2, which is clear evidence for presence of crystalline Co_3O_4 [5, 27, 29]. The IR spectrum of sample (b) displaying two distinct bands that originate from the stretching vibrations of the metal-oxygen bonds [30]. The first band at ~570cm^{-1} is associated with the OB_3 vibration in the spinel lattice where B denotes Co^{3+} in an octahedral hole. The second band at ~662cm^{-1} is attributed to the ABO_3 vibration, where A denotes the Co^{2+} in a tetrahedral hole.

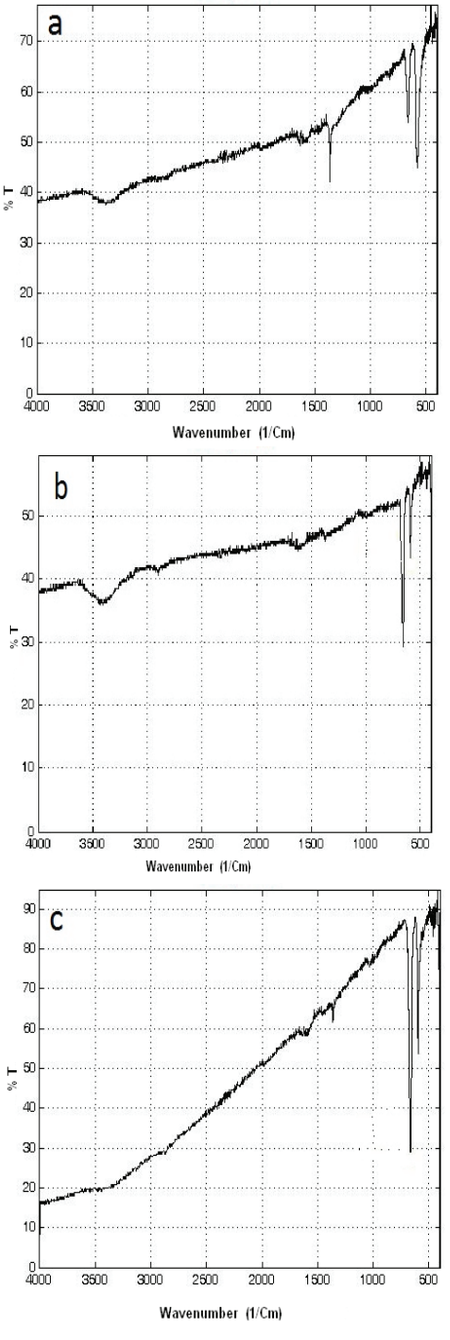

Figure 2 (a, b, c): *IR spectra of tri cobalt tetra oxide (Co_3O_4) obtained from cobalt hydroxide by calcinations (a) at 300°C for 1 hour, (b) at 700°C for 3 hours and (c) cobalt nitrate exposed to microwave energy.*

The peaks at ~1600 cm^{-1} and ~3600 cm^{-1} should be assigned to –OH stretching and bending modes of water respectively which absorbed by the sample or KBr [31-33].

In figure 3 showed FT-IR spectra of cobalt oxide obtained from method III. There are two strong bands at ~564 cm^{-1} and ~661 cm^{-1} due to υ(Co-O) modes which is indicates the presence of crystalline Co_3O_4 and peaks at 1100 cm^{-1} and 3600 cm^{-1} should be assigned to H_2O absorbed by the sample or KBr [27].

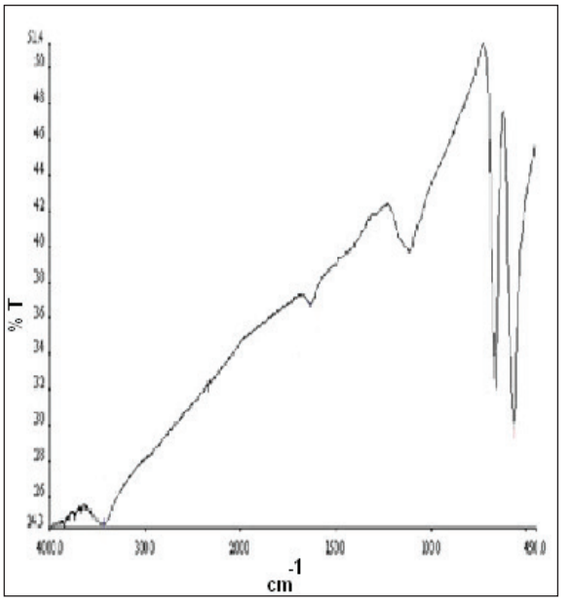

Figure 3: *FT-IR spectra of Co_3O_4 obtained from method III.*

The IR spectra of three samples produced by method I are almost the same,hence two IR spectra illustrated in figure 2 indicated the formation of Co_3O_4 at 300°C and 700°C. The IR spectrum of sample 4 (Figure 2C) also conforms the formation of Co_3O_4 by method II. The FT-IR spectra of the samples produced by method III also clames the formation of Co_3O_4. Since the spectra of the two samples produced by method III are the same, then figure 3 demonstrated one spectra for booth samples.

3.2. XRD

Figure 4 showed the XRD pattern of the final products obtained from methods I (b, c, d, e) and III (a). The XRD patterns indicates the monophasic fcc Co_3O_4 phase is obtained by methods I and III. We can see that the all samples obtained from different methods are Co_3O_4. As shown in figure 4 almost all of peaks intensities of (111), (220), (311), (222), (400), (422), (511), (440), can be perfectly indexed to a pure cubic phase (space group: Fd3m) of Co_3O_4 (a=8.0840A) reported in the literature (JCPDS 74-2120) [27]. The particle size of the investigated Co_3O_4 solids was calculated from the line broadening analysis of some diffraction line of metal oxide phases using Scherrer equation [12]: $D = k.\lambda / \beta_{1/2}.\cos(\theta)$ where k is the Scherrer`s constant (0.89), D the mean crystalline diameter (nm), λ the X-Ray wavelength, $\beta_{1/2}$ is the full width half maximum (FWHM) of the metal oxide diffraction peaks and θ is the diffraction angle.

Inspection of these figures (Figure 4) revealed that the Co_3O_4 solids prepared by different methods and calcined at 300°C, 500°C and 700°C consisted of crystalline Co_3O_4 phase which the quality of crystallinity increases by increase of calcinations temperature. The Co_3O_4 nanoparticles prepared from method I and calcined at 300°C, 500°C and 700°C have crystallite average size of 2 nm, 19 nm and 80 nm respectively which calculated from XRD pattern and Scherrer equation (Table 1).

Table 1: *Variation of Co_3O_4 nanoparticles size by increasing of the calcination temperatures*

Sample	Temperature (°C)	Size (nm)	
		XRD	SEM
Method I	300	2	25
	500	19	76
	700	80	93
Method III	400	18	70

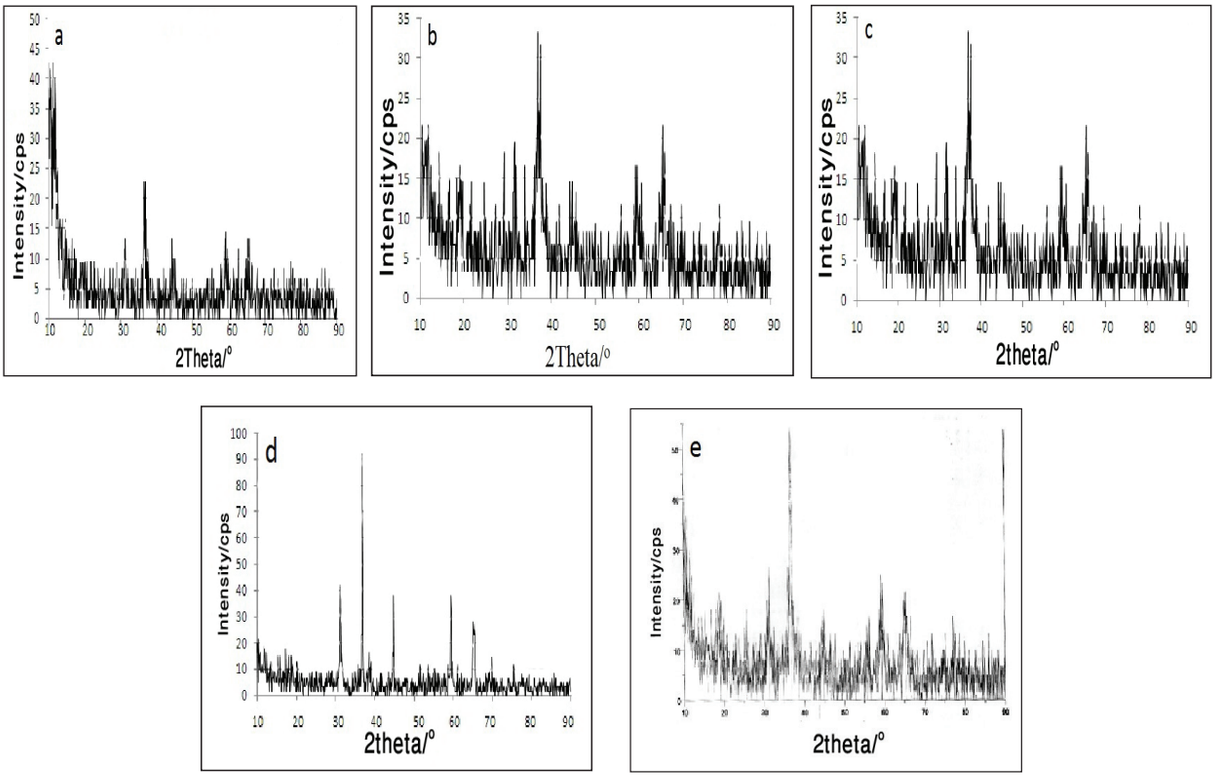

Figure 4 (a, b, c, d, e): *XRD patterns of Co_3O_4 nanoparticles prepared by methods III (a) and I (b, c, d, e).*

The XRD of three samples produced by method I and two samples by method III are illustrated by figure 4. The XRD of samples produced by method II were not taken because their size were above 100 nm that were not considered as good experimental results. The size of samples produced by method I and III were calculated by XRD paterns and scherrer equation are presented in table 1 which implies that the Co_3O_4 nanoparticles produced by method I at 300°C is the best result obtained by this work.

3.3. SEM

The morphology and structure of the product were characterized by scanning electron microscopy (SEM). Figure 5 shows a typical SEM image of Co_3O_4 nanoparticles with various size of 25 nm, 76 nm and 93 nm as increasing with different calcination temperatures of 300°C, 500°C, and 700°C respectively which clearly confirmed by XRD results. Figure 5 (e, f, g) shows SEM images of micro-spheres obtained from the method II. The structure of the micro-spheres is shown obviously in Figure 5(f) which its diameter suggests to be about 1-1.5 μm.

The morphology and structure of the samples produced by method I-III indicate that the smallest nanoparticle size is related to the sample produced by method I which calcinated at 300 °C (Figure 5a) and the largest size is due to samples produced by method II (microwave method).

3.4. Catalytic activity of Co_3O_4 calcined at different temperature

Table 2 shows evolved oxygen volume as a function of time and catalytic activity of Co_3O_4. The catalytic activity calculated from **a=k/(t.m)** equation where a is the activity, k is a constant (mass of 5% hydrogen peroxide for production 100 ml. O_2), t is reaction

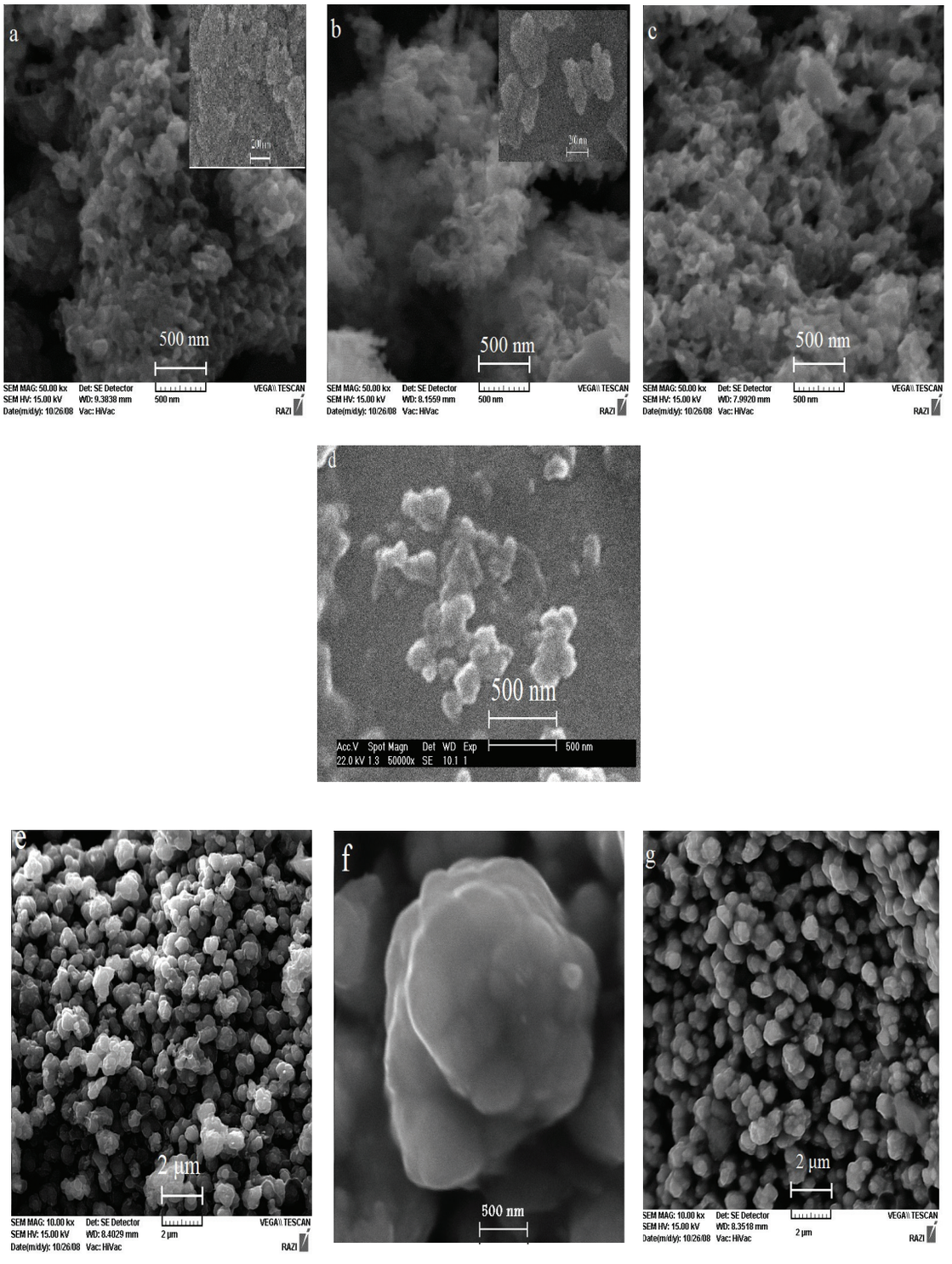

Figure 5 (a, b, c, d, e, f, g): *SEM image of the Co_3O_4 nanoparticles obtained from method I calcined at (a) 300°C, (b) 500°C and (c) 700°C, (d) method III calcined at 400°C for 24 hours and (e, f, g) micro-spheres powder obtained by method II.*

Table 2: *Variation of Co_3O_4 nanoparticles catalytic activity by increasing of the calcination temperatures*

Sample (Co-Precipitation method)	Temperature (^oC)	Rreaction time (s)	Catalytic activity (×100) in k=1
Co_3O_4	300	25	40
Co_3O_4	500	65	15.4
Co_3O_4	700	140	7

time and m is mass of catalyst.
We saw that by increasing of calcinations temperature the catalytic activity of Co_3O_4 nanoparticles was decreased.

4. CONCLUSION

We have clearly demonstrated the importance of the method I for the preparation via precipitation method, and effect of calcination temperatures in morphologies of the Co_3O_4 nanoparticles. It is concluded that the best method for preparation of Co_3O_4 nanoparticles is the co-precipitation method and the best calcinations temperature is 300 ^{o}C. The microwave method is not a suitable method (method II) to prepare Co_3O_4 nanoparticles. We found that at higher temperature, greater nanoparticles were produced which decreased the catalysts specific surface area and at the end decreased catalytic activity in decomposition of hydrogen peroxide.

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