

## A Comparative Study on Spinel Iron-cobalt Oxide Prepared by Co-precipitation and Hydrothermal Routes

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Spinel iron-cobalt oxide was synthesized by coprecipitation and hydrothermal process. The nanostructures of the prepared samples were characterized as functions of the calcination temperature and the hydrothermal synthesis time, using X-ray powder diffractometry (XRD) and nitrogen adsorption-desorption technique (BET, BJH). Using chloride salts as start materials and both of sodium hydroxide and ammonia as precipitating agents; The results show that the  $\text{CoFe}_2\text{O}_4$  obtained has a mesoporous structure with a pore distribution strongly depending on the experimental conditions. The crystallite size and lattice parameter showed a same variation as function of (i) the calcination temperature in the coprecipitation method, (ii) the synthesis time in the hydrothermal process.

**Keywords:** Iron-cobalt spinel, Hydrothermal synthesis, Co-precipitation.

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### 1. INTRODUCTION

Mesoporous materials exhibit interesting properties in many applications such as adsorption, drug delivery, separation process and catalysis. Among them, spinel ferrites nanomaterials have attracted attention due to their stability and also have high potential in various technological applications [1] including ferrofluid technology [2], biomedical applications [3], biosensors [4], photocatalysis [5] and heterogenous catalysis [6].

The simple co-precipitation and hydrothermal methods are known to be suitable for the synthesis of spinel particles with a controlled size and desirable morphology [7,8].

The aim of the present work is to investigate the effect of the preparation method on the structural properties of iron-cobalt spinel oxides. A series of solids  $\text{CoFe}_2\text{O}_4$  were prepared via a co-precipitation method and hydrothermal synthesis process. All samples have been characterized by X-ray powder diffractometry analysis and nitrogen adsorption-desorption technique.

### 2. EXPERIMENTAL

For the co-precipitation preparation method,  $\text{FeCl}_3$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  salts were precipitated, at  $70^\circ\text{C}$ , in an aqueous solution using  $\text{NaOH}$  [9] or  $\text{NH}_4\text{OH}$  [10] as precipitation agent for preparing precursors noted Pr-Na and Pr-NH respectively. The precipitated materials were filtered, washed with bidistilled water and dried overnight at  $80^\circ\text{C}$ . The obtained solids were calcined at different temperatures 500-900 $^\circ\text{C}$ . They will be noted CP-Na-X when the co-precipitation was achieved with  $\text{NaOH}$ , and CP-NH-X when  $\text{NH}_4\text{OH}$  was the precipitating agent, where X stands for the calcination temperature.

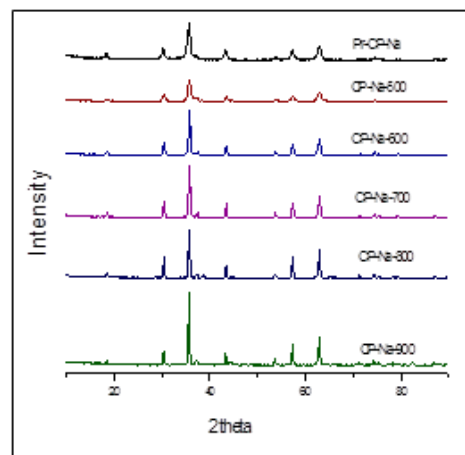
In the hydrothermal synthesis of iron-cobalt mixed oxides [11], the aqueous solutions of iron and cobalt precursors salts were mixed together in a with  $\text{NaOH}$  and autoclaved in a Teflon-lined stainless-steel auto-

clave at  $150^\circ\text{C}$  for different times varied between 2 and 22 hours. The resulting solids were filtered, extensively-washed and then dried at  $80^\circ\text{C}$  for 12 hours. The resultant powders will be designated by HT-Y Where Y stands for the time hydrothermal synthesis.

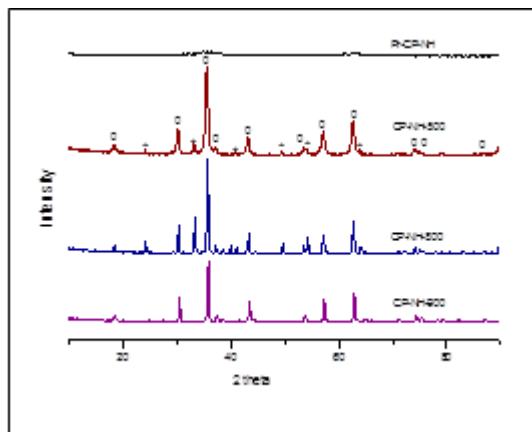
All the samples have been characterized by XRD analysis and nitrogen adsorption-desorption technique.

### 3. RESULTS AND DISCUSSION

XRD patterns of Pr-Na and his calcined samples, depicted in Fig.1, showed that the precursor appeared with a crystallized structure and whatever the calcination temperature, the solids are constituted of a pure spinel phase  $\text{CoFe}_2\text{O}_4$  (JCPDS # 221086). The increase in peak intensities with temperature is due to the increase in crystallinity and particle size during the calcinations process. Fig.2 shows the XRD patterns of the precursor Pr-NH which was amorphous and showed two crystallines phases  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  (JCPDS # 390238) after calcinations.

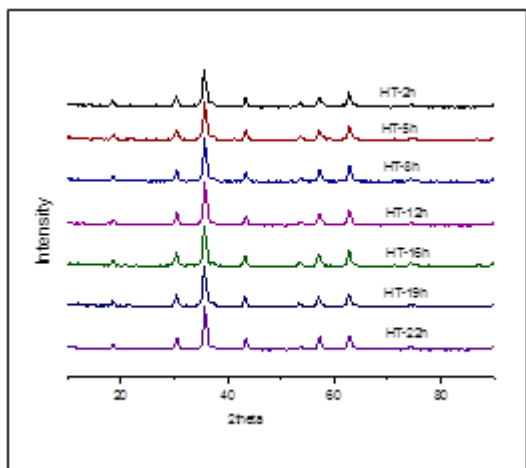


**Fig. 1** – XRD patterns of the samples prepared by co-precipitation with  $\text{NaOH}$



**Fig. 2** – XRD patterns of the samples prepared by coprecipitation with  $\text{NH}_4\text{OH}$  0 :  $\text{CoFe}_2\text{O}_4$  \* :  $\text{Fe}_3\text{O}_4$

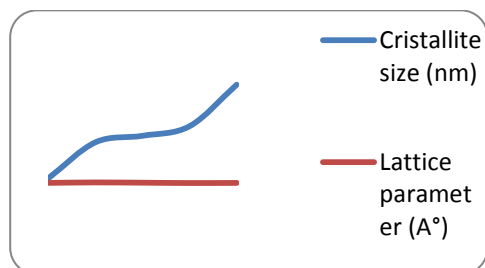
Diffraction patterns of the hydrothermal synthesized powders ( Fig. 3 ) are characteristic of cubic spinel structure and the absence of extra peaks evidence phase purity.



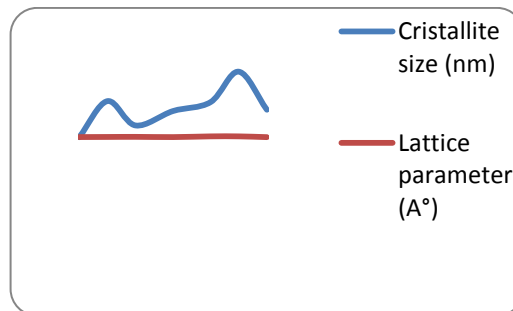
**Fig. 3** – XRD patterns of the samples prepared by hydrothermal synthesis process

The values of crystallite size and lattice parameter were calculated for the corresponding phases obtained in Fig. 1 and Fig. 3 and are plotted, respectively, in Fig. 4 and Fig. 5.

The Fig.4 shows the calcination temperature ( $^{\circ}\text{C}$ ) dependence of the crystallite size and lattice parameter and the Fig.5 shows also the hydrothermal synthesis time (h)dependence with the crystallite size e and lattice parameter .

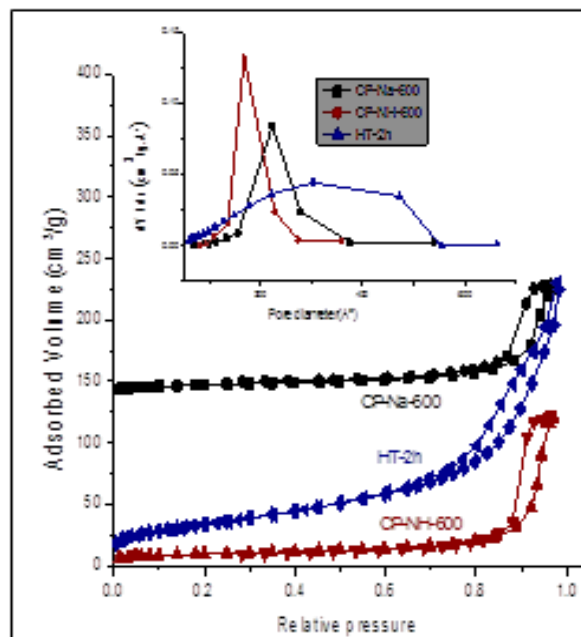


**Fig. 4** – Calcination temperature ( $^{\circ}\text{C}$ ) dependence of the crystallite size and lattice parameter



**Fig. 5** – Hydrothermal synthesis time (h) dependence of the crystallite size and lattice parameter

The results of BET analysis, for three selected samples, are reported in Table 1, noticeable difference was observed between the hydrothermal synthesized sample and the coprecipitated one. The HT-2H solid had the highest surface area ( $122.95 \text{ m}^2 \text{ g}^{-1}$ ) followed by CP-NH-600 ( $33.26 \text{ m}^2 \text{ g}^{-1}$ ). In contrast, the sample CP-Na-600 exhibit a lower surface area ( $27.92 \text{ m}^2 \text{ g}^{-1}$ ). The adsorption-desorption isotherms are represented in Fig.6, all the solids obtained were typical for mesoporous materials.



**Fig. 6** – Adsorption-desorption isotherms and pore distribution

**Table 1** – BET analysis results

Sample	BET surface area( $\text{m}^2/\text{g}$ )	Micropore volume( $\text{cm}^3/\text{g}$ )
CP-Na-600	27.92	0.003118
CP-NH-600	33.26	0.004917
HT-2h	122.95	0.000184

We can verify by these isotherms that the samples prepared via co-precipitation present isotherms type H1 hysteresis loop according to BDDT/IUPAC classification [12] without saturation of capillary condensation and hysteresis closure loop at  $P/P_0 = 0.85$ . The hydro-

thermal synthesized powder shows isotherm type H3 and the hysteresis closure loop occurs at a relative pressure of about  $P/P_0 = 0.75$  and presents a large pore distribution in comparison with the co-precipitation prepared materials.

#### 4. CONCLUSION

Structural and textural properties of spinel iron-cobalt, prepared by co-precipitation method and hydro-

thermal synthesis process, were investigated. The results show the possibility of synthesizing, by the two routes, crystalline monophasic particles of cobalt ferrite using iron and cobalt chlorides as precursors and NaOH as precipitant. This study also shows a correlation of some parameters such as crystallite size, pore distribution and specific surface area, which can influence magnetic and catalytic properties of the materials.

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