

## Cation Distribution Tuning of Solution Combusted $\text{CoFe}_2\text{O}_4$ Powders

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**Abstract:** In this work, the different fuels (citric acid, glycine and urea) were used for solution combustion synthesis of  $\text{CoFe}_2\text{O}_4$  powders. X-ray diffraction, Raman spectroscopy, electron microscopy and vibrating sample magnetometry techniques were employed for characterization of phase evolution, cation distribution, microstructure and magnetic properties of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders. Single phase  $\text{CoFe}_2\text{O}_4$  powders with partially inverse structure in which the  $\text{Co}^{2+}$  cations are distributed in both tetrahedral and octahedral sites were synthesized by the citric acid, glycine and urea fuels. The as-combusted  $\text{CoFe}_2\text{O}_4$  powders by the citric acid fuel exhibited the highest inversion coefficient. The crystallite size of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders synthesized by urea fuel was 15 nm, increased to 41 and 52 nm for the glycine and citric acid fuels, respectively. Furthermore, the solution combusted  $\text{CoFe}_2\text{O}_4$  powders showed ferromagnetic behavior with saturation magnetization of 61.9, 63.6 and 41.6 emu/g for the citric acid, glycine and urea fuels, respectively. The high crystallinity and particle size of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using glycine fuel led to the highest magnetization and the moderate coercivity.

**Keywords:** Fuel, Cation distribution, Inversion coefficient, Magnetic properties;

### 1. INTRODUCTION

Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) as a spinel magnetic ferrite has been considered as well-known material for electronic devices and magneto-optical recording media due to its moderate saturation magnetization and high magnetocrystalline anisotropy [1, 2]. High surface area  $\text{CoFe}_2\text{O}_4$  powders with the excellent chemical stability and electrochemical properties have been found great potential applications in energy storage, catalysis, sensor, water purification, etc. [3-5].

Synthesis method strongly influences on magnetic, electrical and electrochemical properties of cobalt ferrite powders. Various synthesis methods such as hydrothermal, coprecipitation, thermal decomposition and solution combustion have been extensively applied for preparation of  $\text{CoFe}_2\text{O}_4$  powders [6-9]. However, solution combustion synthesis (SCS) has been attracted a great attention for its simplicity, energy- and time-saving and environmentally friendliness [10]. SCS involves a redox reaction between oxidizer (metal salts such as nitrates, sulfates, carbonates, etc.) and fuel (usually urea, glycine, citric acid, etc.). The

redox reaction initiates at moderate low temperatures ( $\sim 150\text{--}200^\circ\text{C}$ ). However, the released heat of combustion reaction leads to propagation of a rapid high temperature ( $1000\text{--}3000^\circ\text{C}$ ) reaction wave in a self-sustained manner, causing the formation of solid product without any additional energy [11, 12]. The initial molecular level mixing of cations induced by complex formation helps to achieve a more homogeneous precursor which is beneficial for preparation multicomponent compounds such as superconductors, spinels, garnets, etc. [13]. The as-combusted products exhibit high porosity and high specific surface area due to the liberation of a large amount of gaseous products [13, 14]. However, powder characteristics such as phase, morphology, particle size and surface area are greatly dependent on fuel type, fuel/oxidizer ratio ( $\phi$ ), pH, salt additives, etc. [15-19]. For example, the amount of released gases products and combustion temperature are mainly related to the fuel characteristics such as solubility, decomposition temperature and reactivity [20]. Among of all types of fuel, the urea and glycine are popular fuels due to their high solubility in water, low decomposition temperature ( $< 400^\circ\text{C}$ ), readily available and low cost [18]. The

citric acid fuel has been attracted a great attention due to its high exothermicity and coordination ability [21]. Lazarova et al. [22] showed the as-combusted nickel ferrite powders using  $\text{NH}_2$ -contained fuels (e. g. urea and glycine) had the larger particle size and higher aggregation ability in comparison with pure carbohydrates fuels (e. g. glucose and sucrose).

In this work, we reported the role of the stoichiometric amount of various fuels (urea, glycine and citric) on phase evolution, cation distribution, microstructure and magnetic properties of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders. The distribution of  $\text{Co}^{2+}$  cations in tetrahedral and octahedral sites were dependent on fuel type which tuned the saturation magnetization.

## 2. EXPERIMENTAL PROCEDURE

The precursor of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ), urea ( $\text{CO}(\text{NH}_3)_2$ ) and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) were purchased from Merck Co..

The required amounts of ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and fuel were dissolved in the distilled water. The fuels were glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ), urea ( $\text{CO}(\text{NH}_3)_2$ ) and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) which were used at fuel to oxidant ratio of 1 ( $\phi=1$ ). After homogenization, the mixture was poured into a dish and heated till to transform into a gel and ignited by further heating up to  $250^\circ\text{C}$  on a hot plate. The resulted powders were hand-crushed with a pestle.

Raman analysis was performed on powders by WiTec Alpha 300R instrument (Nd:YAG laser source:  $\lambda = 532\text{ nm}$  and  $0.7\text{ Mw}$  power, and range:  $100\text{--}900\text{ cm}^{-1}$ ).

Phase evolution was analyzed by PANalytical X-ray diffractometer (XRD) using monochromatic  $\text{CuK}\alpha$  radiation. The average crystallite size was also calculated from the width (311) peak using Scherrer's equation. The morphology and microstructure of the powders were observed by TESCAN Vega II field emission scanning electron microscopy.

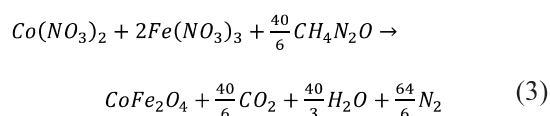
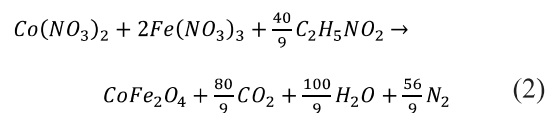
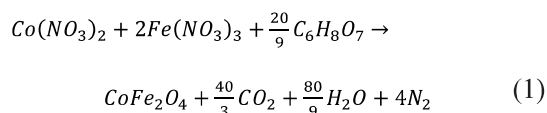
A vibrating sample magnetometer (Meghnatis Daghigh Kavir Co., Iran) was also employed to measure the magnetic properties of cobalt ferrite

powders at room temperature.

All of the thermodynamic calculations in this research were performed using the FactSage 6.1 software [23].

## 3. RESULTS AND DISCUSSION

The redox processes for stoichiometric mixture that are taking place during combustion reaction can be written according to Eqs. (1) to (3):



The stoichiometric mixture does not require atmospheric oxygen for complete fuel oxidation, leading to the maximum adiabatic combustion temperature [13, 24]. The adiabatic combustion temperature ( $T_{\text{ad}}$ ) were calculated by FactSage software for synthesis of cobalt ferrite. The maximum adiabatic combustion temperature is 1796, 1668 and 1537 K using citric acid, glycine and urea fuels, respectively [25].

XRD patterns of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using citric acid, glycine and urea fuels are shown in Fig. 1. The indexed peaks as (220), (311), (222), (400), (422), (511) and (440) of the cubic spinel structure confirm the direct formation of single phase  $\text{CoFe}_2\text{O}_4$  after combustion reaction without further heat treatment. The wider and noisy diffraction peaks for urea fuel are due to its small crystallite size and lower crystallinity originated from lower adiabatic temperature. Furthermore, the weak coordination ability of glycine fuel results in

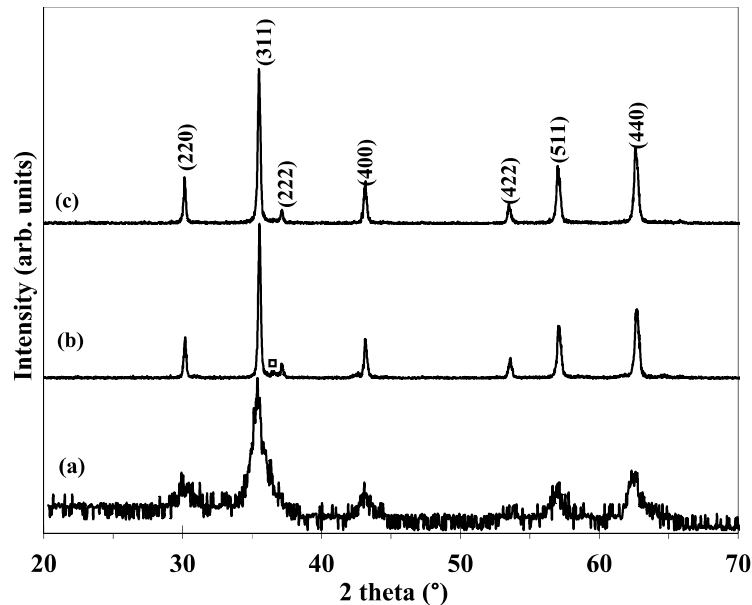


Fig. 1. XRD patterns of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using (a) urea, (b) glycine and (c) citric acid fuels ( $\square$ :CoO).

Table 1. Cation distribution and crystallite size of the as-combusted  $\text{CoFe}_2\text{O}_4$  as a function of fuel type.

| Fuel        | I220/I400 |       | I422/I400 |       | Cation distribution                                                                                    | Crystallite size (nm) |
|-------------|-----------|-------|-----------|-------|--------------------------------------------------------------------------------------------------------|-----------------------|
|             | Obs.      | Calc. | Obs.      | Calc. |                                                                                                        |                       |
| Urea        | 1.10      | 1.26  | 0.11      | 0.21  | $(\text{Co}_{0.09}\text{Fe}_{0.91})_{\text{A}}[\text{Co}_{0.09}\text{Fe}_{1.91}]_{\text{B}}\text{O}_4$ | 15                    |
| Glycine     | 1.21      | 1.31  | 0.31      | 0.39  | $(\text{Co}_{0.05}\text{Fe}_{0.95})_{\text{A}}[\text{Co}_{0.95}\text{Fe}_{1.05}]_{\text{B}}\text{O}_4$ | 41                    |
| Citric acid | 1.65      | 1.71  | 0.35      | 0.42  | $(\text{Co}_{0.03}\text{Fe}_{0.97})_{\text{A}}[\text{Co}_{0.97}\text{Fe}_{1.03}]_{\text{B}}\text{O}_4$ | 52                    |

some impurity CoO phase. The crystallite size of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using urea fuel is 15 nm, increases to 41 and 52 nm for glycine and citric acid fuels, respectively, as listed in Table 1. The higher crystallite sizes using citric acid fuel can be attributed to its higher adiabatic combustion temperature.

The cation distribution can be determined by analyzing of XRD patterns by Bertaut method [26]. This method compares the observed intensity ratios with the calculated intensity ratios for exploring the minimum of agreement factor (R) by varying the cation distribution in the supposed structure [27]:

$$R = \left( \frac{I_{hkl}}{I_{\bar{h}\bar{k}\bar{l}}} \right)_{\text{obs.}} - \left( \frac{I_{hkl}}{I_{\bar{h}\bar{k}\bar{l}}} \right)_{\text{calc.}} \quad (4)$$

The relative integrated intensity of a given diffraction line from powder specimens in a diffractometer with a flat plate sample holder can be calculated by following formula [28]:

$$I_{hkl} = |F_{hkl}|^2 P L_p \quad (5)$$

which P is the multiplicity factor and  $L_p$  is the Lorenz-polarization factor which depends only on Bragg's diffraction angle  $\theta$ , as follows [29]:

$$L_p = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos 2\theta} \quad (6)$$

and  $F_{hkl}$  is the structure factor which can be described for 220, 400 and 422 planes as follows [30]:

$$F_{220} = -8F_A + 16f_O(\cos 8\pi u - 1) \quad (7)$$

$$F_{400} = 8(F_A - F_B + 4f_O \cos 8\pi u) \quad (8)$$

$$F_{422} = -8F_A + 8f_O(\cos 16\pi u - 2\cos 8\pi u + 1) \quad (9)$$

which  $u$  is oxygen positional parameter,  $f_O$  is scattering factor of oxygen atom and  $F_A$  and  $F_B$  are the total scattering factor of atoms in A- and B-sites, respectively. For  $(\text{Co}_{1-\delta}\text{Fe}_\delta)_A[\text{Co}_\delta\text{Fe}_{2-\delta}]_B\text{O}_4$ ,  $F_A$  and  $F_B$  can be written as:

$$F_A = (1 - \delta)f_{\text{Co}} + \delta f_{\text{Fe}} \quad (10)$$

$$F_B = \delta f_{\text{Co}} + (2 - \delta)f_{\text{Fe}} \quad (11)$$

which  $f_{\text{Co}}$  and  $f_{\text{Fe}}$  are scattering factors of cobalt and iron atoms, respectively. The thermal correction of diffraction line is no need for spinel structure on account of its high melting point [29]. Some peaks' intensity ratios like I220/I400, I220/I422 and I422/I400 as cation distribution sensitive peaks can be used for determination of the cation distribution in spinel structures [28]. The cation distributions as a function of fuel type are given in Table 1. Cation distribution shows that the as-combusted  $\text{CoFe}_2\text{O}_4$  powders have a partially inverse structure in which the divalent cations ( $\text{Co}^{2+}$ ) are distributed in tetrahedral (A) and octahedral [B] sites. The inversion coefficient ( $\delta$ ) defined as the fraction of  $\text{Fe}^{3+}$  cations in tetrahedral sites (A-sites) depends on fuel type. The highest inversion coefficient ( $\delta=0.97$ ) for citric acid fuel can be attributed to the higher chelatability and adiabatic combustion temperature which promote the cation diffusion.

The theoretical lattice parameter can be calculated by following equation [31]:

$$a_{th} = \frac{8}{3\sqrt{3}}[(r_A + R_O) + \sqrt{3}(r_B + R_O)] \quad (12)$$

where  $r_A$  and  $r_B$  are the radii of tetrahedral and octahedral sites and  $R_O$  is the radius of oxygen ions ( $R_O=1.32 \text{ \AA}$ ). The mean ionic radius of tetrahedral (A) and octahedral [B] sites ( $r_A$  and  $r_B$ ) can be calculated by following relations [31]:

$$r_A = (1 - \delta)r_{\text{Co}^{2+}} + \delta r_{\text{Fe}^{3+}} \quad (13)$$

$$r_B = \frac{1}{2}[\delta r_{\text{Co}^{2+}} + (2 - \delta)r_{\text{Fe}^{3+}}] \quad (14)$$

The radii of tetrahedral and octahedral sites and theoretical ( $a_{th}$ ) and experimental ( $a_{exp}$ ) lattice parameters are presented in Table 2. The agreement between  $a_{th}$  and  $a_{exp}$  indirectly verifies the cation distribution deduced from X-ray intensity calculations [32].

Raman spectra of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders in the range of  $100\text{--}800 \text{ cm}^{-1}$  are shown in Fig. 2. The irreducible representations for spinel ferrite structures with O7h (Fd3m) space group are as follows [33]:

$$\Gamma_{\text{irred}} = A_{1g}(\text{R}) + E_g(\text{R}) + T_{1g} + 3T_{2g}(\text{R}) + 2A_{2u} + 2E_u + T_{1u}(\text{IR}) + 2T_{2u} \quad (15)$$

The  $A_{1g}(\text{R}) + E_g(\text{R}) + 3T_{2g}(\text{R})$  modes are Raman active modes at ambient conditions and the  $T_{1u}$  is only infrared active mode. The  $T_{1g}$ ,  $A_{2u}$ ,  $E_u$  and  $T_{2u}$  are silent symmetry vibration modes. The natural frequency of the Raman active modes was determined by a least square fit with Lorentzian line shape, as illustrated in Fig. 2. Table 3 presents the Raman shifts and their assignments of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders as a function of fuel type. The broadening of the high

**Table 2.** The average ionic radius of the tetrahedral and octahedral sites ( $r_A$  and  $r_B$ ) and experimental ( $a_{exp}$ ) and theoretical ( $a_{th}$ ) lattice parameter.

| Fuel        | $r_A$ (Å) | $r_B$ (Å) | $a_{exp}$ (Å) | $a_{th}$ (Å) |
|-------------|-----------|-----------|---------------|--------------|
| Urea        | 0.654     | 0.6905    | 8.3930        | 8.4003       |
| Glycine     | 0.65      | 0.6925    | 8.3830        | 8.3995       |
| Citric acid | 0.648     | 0.6935    | 8.3983        | 8.3991       |

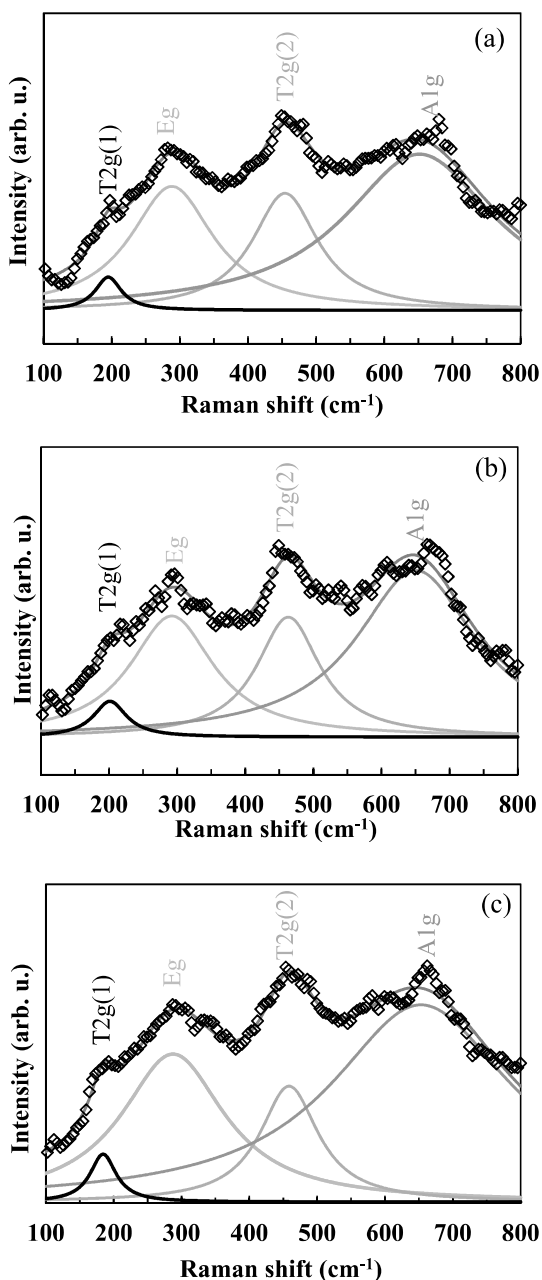


Fig. 2. Raman spectra of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using (a) urea, (b) glycine and (c) citric acid fuels.

frequency modes due to the small crystallite size of  $\text{CoFe}_2\text{O}_4$  powders eliminates low-frequency modes. The motion of oxygen in tetrahedral  $\text{AO}_4$  group (A-site) leads to Raman shifts above  $600\text{ cm}^{-1}$ , while the other low Raman shifts are related to the octahedral  $\text{BO}_6$  group (B-site) [34]. All

Table 3. Raman parameters of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders.

| Fuel        | Assignment |     |        |     |
|-------------|------------|-----|--------|-----|
|             | T2g(1)     | Eg  | T2g(2) | A1g |
| Urea        | 194        | 288 | 458    | 653 |
| Glycine     | 201        | 291 | 463    | 650 |
| Citric acid | 184        | 285 | 451    | 649 |

modes of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using citric acid fuel are shifted toward the lower wave number region, may be due to its highest inversion coefficient.

The microstructures of as-combusted  $\text{CoFe}_2\text{O}_4$  powders using citric acid, glycine and urea fuels are shown in Fig. 3. For urea fuel, the particles are tightly agglomerated in the range of 5 and  $20\text{ }\mu\text{m}$ . The increase of pH by decomposition of urea induces the precipitation of hydroxides, which aggregate during combustion reaction [18]. However, the particles were sintered using glycine fuel, due to its fast thermal decomposition. The bulky morphology of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using citric acid fuel can be attributed to the establishment of polymeric network between the citrate species, postponing the liberation of gaseous products. It was also reported the  $\text{COOH}$  ligand has lower reactivity than that of  $-\text{NH}_2$  group for releasing gaseous products, leading to the bulky microstructure of the as-combusted powders using citric acid fuel [20].

Fig. 4 shows the magnetization curves of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders by various fuels at  $\phi=1$ . The saturation magnetization ( $M_s$ ), remanence ( $M_r$ ) and coercivity ( $H_c$ ) values are presented in Table 4. The as-combusted  $\text{CoFe}_2\text{O}_4$  powders using glycine fuel exhibit the highest saturation magnetization ( $63.9\text{ emu/g}$ ), in spite of

Table 4. Magnetic properties of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders

| Fuel        | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ (Oe) |
|-------------|---------------|---------------|------------|
| Urea        | 41.6          | 11.8          | 847        |
| Glycine     | 63.6          | 32.5          | 1113       |
| Citric acid | 61.9          | 27.4          | 1335       |

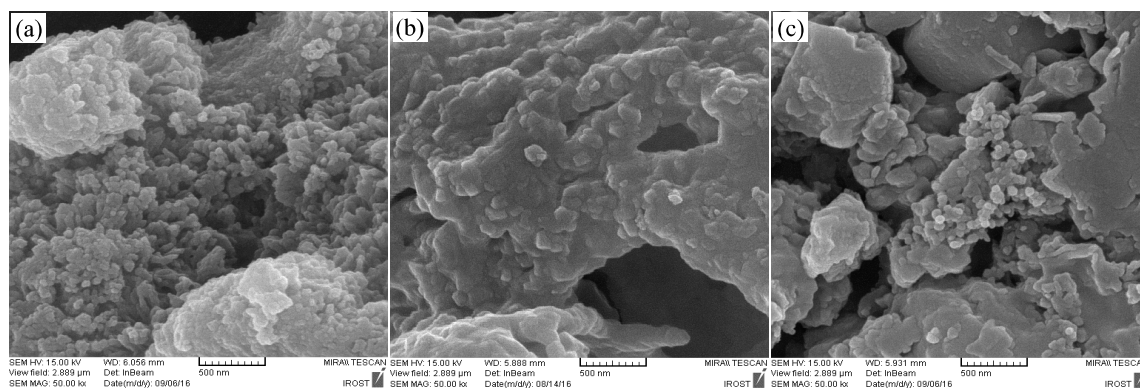


Fig. 3. SEM micrographs of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using (a) urea, (b) glycine and (c) citric acid fuels

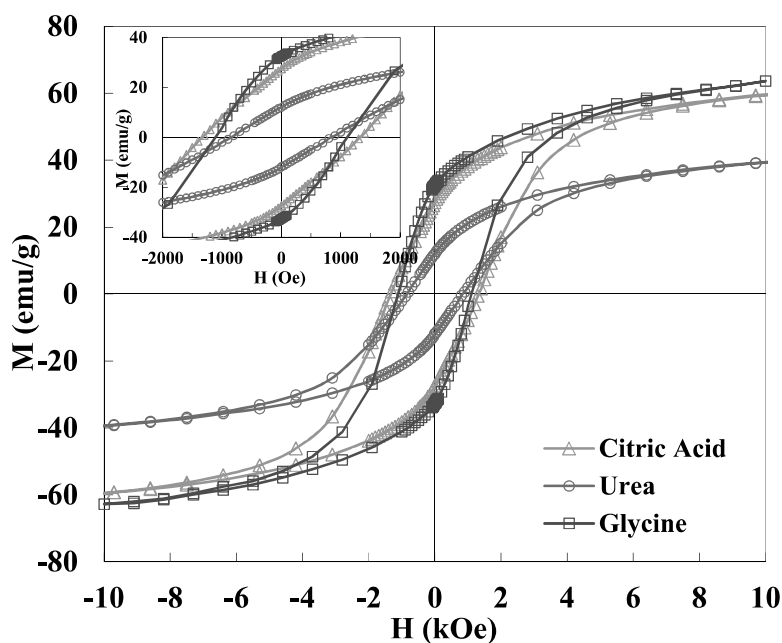


Fig. 4. Hysteresis loops of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using different fuels.

some impure  $\text{CoO}$  phase. This can be attributed to the higher crystallinity originated from higher combustibility of glycine [13]. In spite of the higher purity and adiabatic temperature for citric acid fuel, the saturation magnetization is slightly lower than that for glycine fuel, may be due to its highest inversion coefficient. The cubic spinel ferrites have two different sublattices for magnetic ions, i.e., tetrahedral (A) and octahedral [B] sublattices. The superexchange interaction

between the magnetic ions in the A and B sublattices controls the magnetic order in magnetic spinel ferrite. According to the Neel model, A–B superexchange interactions are predominant over intrasublattice A–A and B–B interactions and the saturation magnetization is given by the vector sum of the net magnetic moments of the individual A and B sublattices [35]. The more  $\text{Fe}^{3+}$  cations with the ionic magnetic moments of  $5_{\mu\text{B}}$  in tetrahedral (A) sites

in the higher inversivity decreases the magnetic moment of the B-site and then the total magnetic moments.

The lowest  $H_c$  of 847 Oe is obtained for the urea fuel, because their crystallite size is smaller than that of single-domain size limit ( $\sim 40$  nm). The prevailing of the thermal energy on the anisotropy energy for  $D < 40$  nm leads to the decrease of  $H_c$  [36,37]. The solution combusted  $\text{CoFe}_2\text{O}_4$  powders usually exhibit the higher saturation magnetization in comparison with the other synthetic methods due to their high crystallinity originated from high adiabatic combustion temperature. However, the coercivity is strongly related to the particle size, making the comparison difficult.

#### 4. CONCLUSION

Single phase  $\text{CoFe}_2\text{O}_4$  powders have been prepared by solution combustion method using urea, glycine and citric acid as fuel. The cation distribution in tetrahedral and octahedral sites determined by XRD analysis was strongly dependent on fuel type. The higher coordination ability of citric acid toward cations resulted in the highest inversion coefficient. The sintered microstructure of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders using glycine fuel was attributed to its fast combustion and high adiabatic temperature. Furthermore, the magnetic properties of the as-combusted  $\text{CoFe}_2\text{O}_4$  powders can be adjusted by the fuel type through crystallinity, crystallite size and cation distribution.

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