



Preparation of Polymer Foam Magnesium Ferrite Nano-Materials by Polymerization Phenomena of Metal Ions in Aqueous Solution

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In the present investigation, the polymer foam magnesium ferrite/hematite, $\text{MgFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ and magnesium ferrite (MgFe_2O_4) were prepared by using magnesium oxide (MgO) and ferric chloride ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) as starting materials with assisted ultrasonic dispersing technology in the aqueous solution. FTIR, XRD, SEM and TG-DTG-DTA analysis indicated that the transformation of $\text{MgFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ to MgFe_2O_4 was obtained by adjusting the molar ratio of Mg/Fe selectively or the pH value of aqueous solution. The grain size and morphology of the resultant nano-crystalline were also strongly affected by the molar ratio of Mg/Fe selectively, the pH value of aqueous solution and the calcinations temperature. The forming mechanism of polymer foam MgFe_2O_4 can be explained according to the polymerization phenomena of metal ions in aqueous solution. In this study, not any additives or modifiers were used, which demonstrates the potential application of MgFe_2O_4 in various field.

Keywords: Magnesium ferrite, Polymer foam, Hematite, Polymerization phenomena, Metal ions.

INTRODUCTION

Magnesium ferrite (MgFe_2O_4) was regarded as an important candidate of the spinel family which have a cubic structure of normal spinel-type. Applications such as in ferro-fluid, high-density recording media, heterogeneous catalysis, adsorption, humidity and gas sensors and magnetic technologies *etc.* have been developed as a result of its interesting magnetic and electrical properties combined with chemical and thermal stability¹. Furthermore, the potential applications in drug and bio-molecules carriers, or bio-inspired technology have attracted much attention by coating or layered on the magnesium ferrite core².

Magnesium ferrite (MgFe_2O_4) can be prepared by conventional ceramic method (ball milling)³⁻⁷, polymeric precursor method⁸, sol-gel method⁹⁻¹², oxygen-plasma-assisted molecular beam epitaxy¹³, combustion reaction method¹⁴⁻¹⁸, layered precursor method¹⁹, low-temperature sol-gel auto-combustion method²⁰, co-precipitation method²¹⁻²⁴, electro-spinning method²⁵, supercritical hydrothermal reaction²⁶, a molten salt synthesis method²⁷, a one-pot solvo-thermal route²⁸, PEG assisted micro-emulsion method^{29,30}. Various wet-method have been reported for preparing spinel-type ferrite fine particles, in which magnesium salt included magnesium sulfate, magnesium nitrate and hydrated magnesium acetate *etc.* were often used as a starting materials and some of the organic acids

included oleic acid, citric acid, acetic acid and glycine *etc.* so much as surfactant were used as dispersing agent. In additions, some of the alkaline substances included sodium hydroxide, potassium hydroxide, so much as ammonia *etc.* were used as regulator of pH value in aqueous solution³¹⁻³³. However, these surface and pH regulator may be remained in the product, which is unfavourable to the application. Therefore, preparation of MgFe_2O_4 without using any surface and pH regulator is important.

In the present investigation, magnesium oxide (MgO) and ferric chloride ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) were used as starting materials and ultrasonic assisted dispersing were used. The molar ratio of Mg/Fe was selectively to adjust the pH value of aqueous solution. Not any additives or modifiers were used. The behaviour of the synthesized precursor at different pH value was studied. The grain size and morphology of the resultant nanocrystalline were investigated.

EXPERIMENTAL

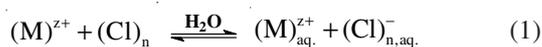
The chemicals used in the synthesis of samples were magnesium oxide powder (MgO) and ferric chloride ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$). Magnesium oxide was dissolved in the distilled water with ultrasonic stirring (frequency 30 Hz and 300 rpm) for 1 h at 50 °C, forming MgO emulsion. $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ was also dissolved in the distilled water in the same condition as mentioned above. Then the FeCl_3 was dropwise added to the prepared MgO

emulsion, after the completion of drop, the reaction was continued for 1 h with ultrasonic stirring at 50 °C. Finally, the precursor were filtered, washed and dried at 100 °C for 4 h and then the formed precursor powders were calcined at 600, 800 and 1000 °C respectively for 2 h in a digital furnace. The X-ray diffraction (XRD) patterns of the resulting products were characterized by a Bruker D8-advance X-ray powder diffractometer with $\text{CuK}\alpha$ radiation ($k = 1.5406 \text{ \AA}$) in the 2 θ range from 10 to 80°. The micrograph of MgFe_2O_4 was examined by direct observation via scanning electron microscope (SEM) model (JSM-5400). The Fourier transformer infrared (FT-IR) patterns of the resulting products were characterized by a Bruker V-70 infrared spectrometer.

RESULTS AND DISCUSSION

pH value measured: The pH value measured as function of time with different molar ratios of (Mg/Fe) was shown in Fig. 1. It can be seen that the pH value measured decrease with increase of reaction time as molar ratio of (Mg/Fe) above 2.5:1 and finally reach a curtained value. The pH value measured decrease and then suddenly down decrease to a certain value as molar ratio of (Mg/Fe) below 2.25:1. On the other hand, the solution shows basic as molar ratio of (Mg/Fe) above 2.5:1 and acidity below 2.25:1 in the reaction at the end. The pH value measured in the reaction at the end as function of molar ratio of (Mg/Fe) was shown in Fig. 2, the S-type curve was clearly obtained. This phenomenon indicated that the reaction was part of alkali neutralization reaction in fact as Fe^{3+} solution was dropped into the MgO emulsion.

TG-DTG-DTA characterization: In aqueous chemistry, water plays a double role. It behaves as a solvent with a high dielectric constant that favours the dissociation of ionic species as:



where M is metal ion. It also behaves as a σ -donor molecule and reacts as a nucleophilic ligand giving solvated species as:

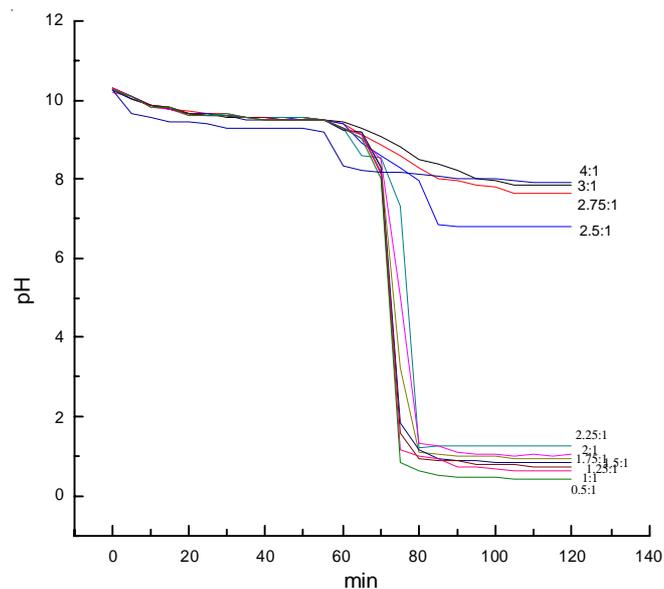


Fig. 1. pH value measured as function of time with different molar ratios of (Mg/Fe)

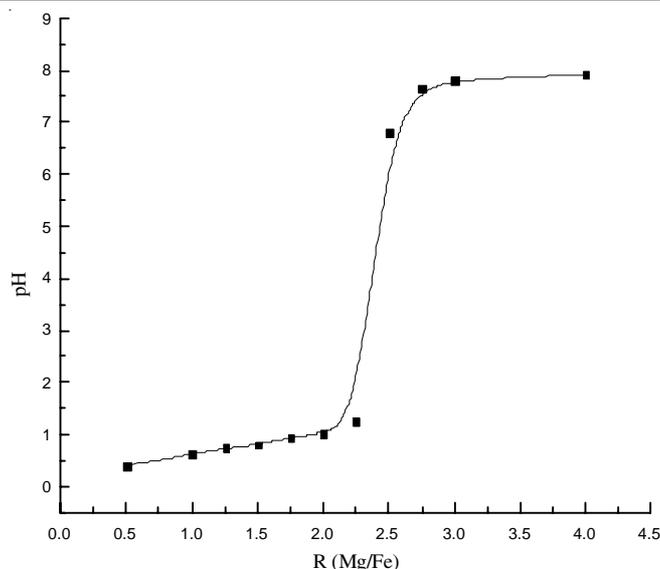


Fig. 2. pH value measured as function of molar ratio of (Mg/Fe)

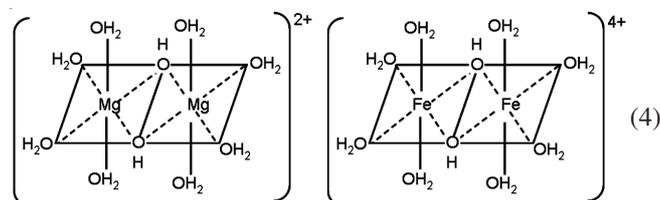


when the pH value increase,



where h is the hydrolysis ratio.

Here, we consider that the magnesium and ferrite hydrated ion are formed in aqueous solution. These hydrated ions in aqueous solution take place ionic polymerization, forming generally recognized as magnesium or iron oxide octahedral or tetrahedron structure:



Sequentially, the back-to-back connection or cross linking of the magnesium or iron oxide octahedral or tetrahedron structure will formed as a results of share of the hydroxyl ion or the H_2O . The polymerization phenomena of metal ions in aqueous solution took place, the compound of magnesium and iron oxide architecture in nanospace were obtained, then the polymer foam of MgFe_2O_4 will be prepared after calcination.

Thermal decomposition of the precursor with Mg/Fe molar ratio 1.75 ($\text{pH} = 0.95$) consists of two steps as shown in Fig. 3. In the TG-DTA curve of the dried gel ($\text{pH} = 0.95$), the first weight loss represents the water vaporization of O-H groups and the second weight loss corresponds with the decomposition of Cl^- ions. Therefore, it is confirmed that the amount of heat produced depends on the hydrolysis temperature and time, which is a key factor affecting the size and morphology of the particles.

X-ray analysis: The XRD patterns of the powders heat-treated at 800 °C with different Mg/Fe molar ratios from 1.25 to 4 are shown in Fig. 4. The diffraction peaks at 2θ values of 30.1, 35.5, 43.1, 53.5, 57.1 and 62.6, are corresponding to (220), (311), (400), (422), (511) and (440) planes, respectively,

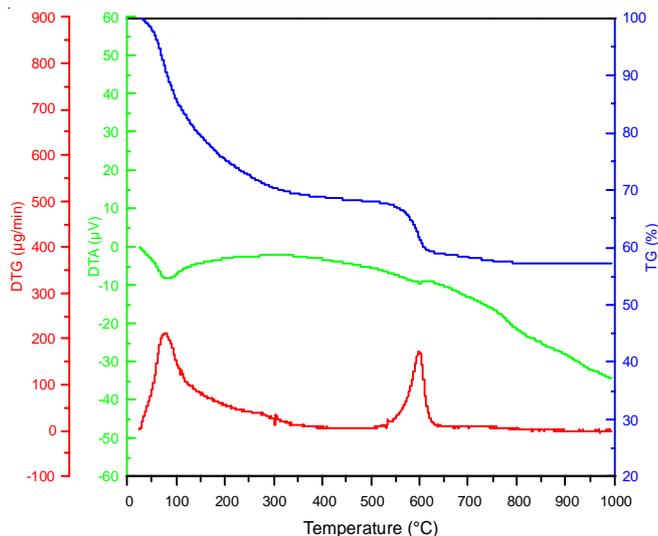


Fig. 3. TG-DTG-DTA curves of precursor sample at Mg/Fe molar ratio 1.75:1

which provide a clear evidence for the formation of the spinel structure of the magnesium ferrites as Mg/Fe molar ratio 4:1. The diffraction peaks at 24.1, 33.1, 35.6, 40.8, 49.5, 54.1, 57.6, 62.5 and 64.0, are corresponding to (012), (104), (110), (113), (024), (116), (122), (214), (300), (010) and (220) planes of

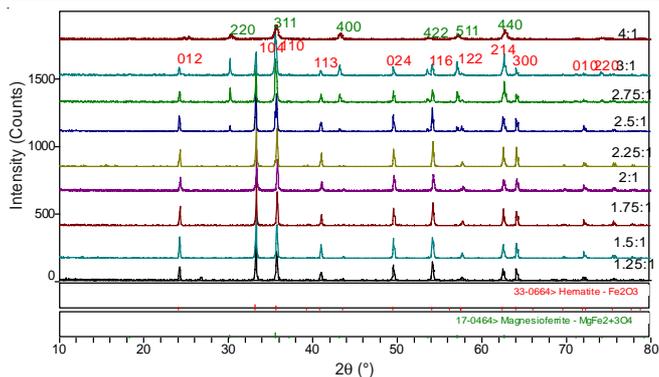


Fig. 4. X-ray diffraction patterns of MgFe₂O₄ samples at different Mg/Fe molar ratios

rhombohedral α -Fe₂O₃ and (220), (400) and (511) *etc.*, corresponding to planes of the spinel structure of the magnesium ferrites existed and increased as Mg/Fe molar ratio from 2.5:1 to 3.0:1. And only (311), (422) and (440) coexisted as Mg/Fe molar ratio from 1.25:1 to 2.25:1. These results show clearly that the transformation of MgFe₂O₄/ α -Fe₂O₃ to MgFe₂O₄ as Mg/Fe molar ratio from 1.25:1 to 4:1.

SEM observation: Fig. 5 shows the SEM images of MgFe₂O₄/ α -Fe₂O₃ after calcinations at 800 °C for 2 h. It can

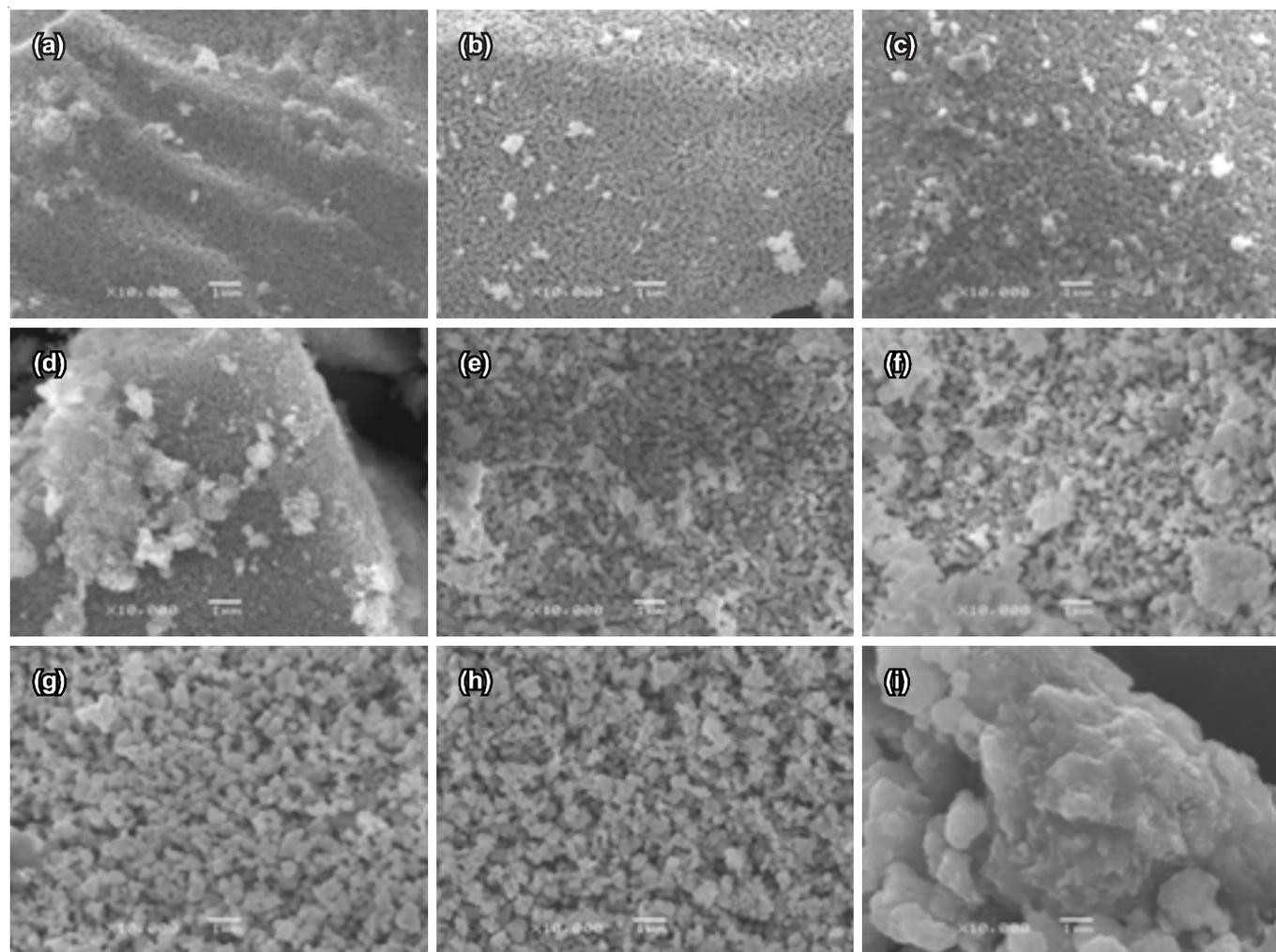


Fig. 5. SEM images of MgFe₂O₄/ α -Fe₂O₃ samples at different Mg/Fe molar ratios (a: 1.25:1, b: 1.5:1, c: 1.75:1, d: 2.0:1, e: 2.25:1, f: 2.5:1, g: 2.75:1, h: 3.0:1, i: 4.0:1)

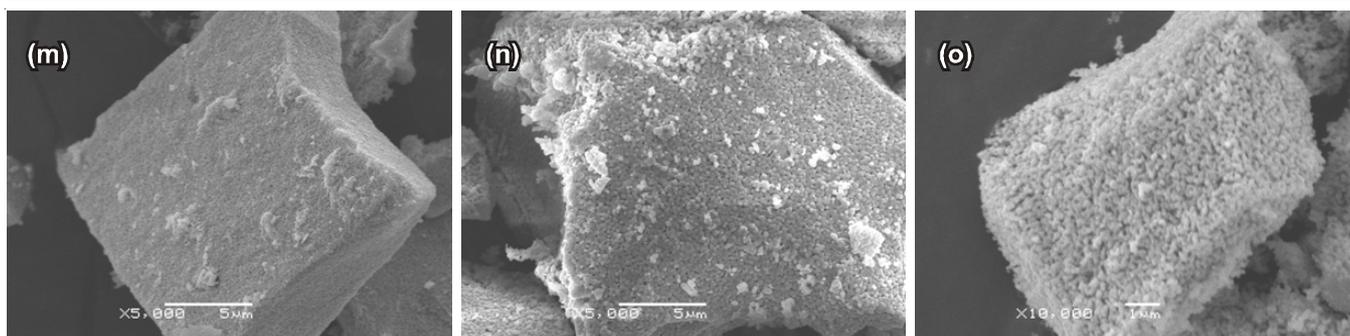


Fig. 9. SEM images of $\text{MgFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ samples calcined at $800\text{ }^\circ\text{C}$ when the Mg/Fe molar ratio (m: 1.25:1, n: 1.75:1, o: 2.0:1)

of Mg/Fe molar ratio from 1.25:1 to 1.75:1. It is confirmed the transformation of the $\text{MgFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ phases in Fig. 8.

Polymer foam: The SEM images of $\text{MgFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ samples calcined at $800\text{ }^\circ\text{C}$ when the Mg/Fe molar ratio is 1.25:1, 1.75:1 and 2.0:1 were shown in Fig. 9 (m, n, o), respectively. It can be seen that perfect polymer foam have been obtained. The particle diameter increases with the increase of Mg/Fe molar ratio from 1.25:1 to 2.0:1. On the other hand, proves that the polymerization phenomena of metal ions in aqueous solution increase with the increase of pH value, or, metals irons transform from low polymer to high cohesion with Mg/Fe molar ratio change from 1.25:1 to 2.0:1.

VSM study: Hysteresis loop of MgFe_2O_4 samples calcined at $800\text{ }^\circ\text{C}$ prepared at the Mg/Fe molar ratio from 1.25:1 to 3.0:1 are shown in Fig. 10. It is clearly seen that the value of saturation magnetization (M_s) of the sample prepared at the Mg/Fe molar ratio from 1.25:1 to 2.25:1 is smaller than that prepared at the Mg/Fe molar ratio from 2.5:1 to 3.0:1, the variation in magnetization could be understood as a result of the formation of the spinel structure of the magnesium ferrites prepared at the Mg/Fe molar ratio from 2.5:1 to 3.0:1 and the value of saturation magnetization (M_s) of the sample increase with the Mg/Fe molar ratio from 2.5:1 to 3.0:1. It is also found

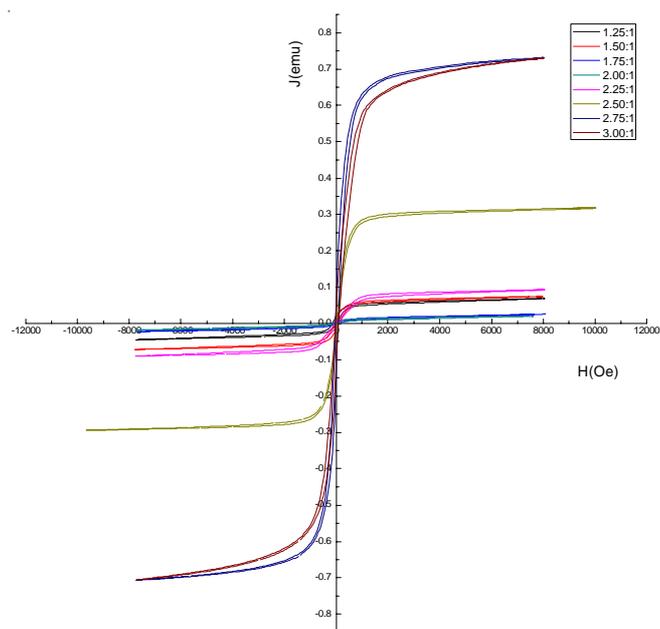


Fig. 10. Hysteresis loop of MgFe_2O_4 samples calcined at $800\text{ }^\circ\text{C}$ prepared at different molar ratio of Mg/Fe

that the coercivity (H_c) of the sample prepared at the Mg/Fe molar ratio from 1.25:1 to 2.25:1 is smaller than that prepared at the Mg/Fe molar ratio from 2.5:1 to 3.0:1, the change in coercivity may be attributed to the change in size of the ferrite particle, as particle size reached the critical size the coercivity go to zero and the grain becomes super-paramagnetic.

Conclusion

The magnesium ferrite/hematite, $\text{MgFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ and magnesium ferrite, MgFe_2O_4 were prepared by using magnesium oxide (MgO) and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) as starting materials with assisted ultrasonic dispersing technology in the aqueous solution. The transformation of $\text{MgFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ to MgFe_2O_4 was obtained by adjusting the molar ratio of Mg/Fe selectively or the pH value of aqueous solution. The grain size and morphology of the resultant nano-crystalline are strongly affected by the Mg/Fe selectively or the pH value of aqueous solution and the calcinations temperature. The forming mechanism of polymer foam MgFe_2O_4 can be explained according to the polymerization phenomena of metal ions in aqueous solution. In this study, not any additives or modifiers were used, demonstrating the potential application of MgFe_2O_4 in various field. The value of saturation magnetization (M_s) of the sample prepared at the Mg/Fe molar ratio from 1.25:1 to 2.25:1 is smaller than that prepared at the Mg/Fe molar ratio from 2.5:1 to 3.0:1, the coercivity (H_c) of the sample prepared at the Mg/Fe molar ratio from 1.25:1 to 2.25:1 is also smaller than that prepared at the Mg/Fe molar ratio from 2.5:1 to 3.0:1.

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