Formation of CaFe$_2$O$_4$ porous structure by addition of Zr in malic acid complex

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The effect of Zr addition into malic acid complex was examined for the purpose of the improvement of microstructure and specific surface area of CaFe$_2$O$_4$. The CaFe$_2$O$_4$ phase could be obtained for both unadded and Zr-added (5 and 10 mol % with respect to Fe) system by calcination of precursor derived from malic acid complex at 700°C which is almost 200°C lower than that of conventional solid-state reaction method. Among the examined products, only the 5 mol % Zr-added product revealed characteristic smaller grains connected three dimensional porous structures resulting in higher specific surface area compared with unadded and 10 mol % Zr-added products. XPS measurements revealed that there are no notable changes in valence state for all constituent elements. The obtained final product of 5 mol % Zr-added CaFe$_2$O$_4$ is worth further investigate for various application from a view point of improved higher specific surface area and characteristic microstructure as well as the functionality of the material itself.

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CaFe$_2$O$_4$ has been known as a functional material applicable for electrochemical devices, oxidation catalysts, photocatalysts, and gas adsorbents. In these applications, especially for surface-related function driven devices such as catalysts, morphology, microstructure, and surface area are important factor to enhance the performance of CaFe$_2$O$_4$. As for the photocatalysts, several oxide-based photocatalysts require higher temperature calcination resulting in lower surface area without microstructural characteristics. From a view point of p-type semiconducting material, CaFe$_2$O$_4$ might be a candidate as a photocatalyst when some problems such as lower surface area as well as microstructural control were solved. On the other hand, the method using organic acid complex derived precursor is easier in microstructure control than that of conventional solid-state reaction method. Additionally, the formation temperature of the objective product often lowered than that of solid-state reaction due to its fine mixture of starting materials in atomic level. As for the preparation of CaFe$_2$O$_4$, the forming temperature could be lower at least 200°C results in 700°C by adopting organic acid complex method, and the specific surface area (SSA) of the obtained CaFe$_2$O$_4$ powder was approximately five times larger than that of the product obtained by a solid-state reaction. On the other hand, however, microstructure control of the malic acid complex derived products has not been examined. There are some strategies for microstructure control of CaFe$_2$O$_4$, i.e., the selection of complex formable acids, the addition of another element, and so on. Among them, the addition of another element into CaFe$_2$O$_4$ is thought to affect the sintering behavior as well as the character of products. Especially, when the additional element was added or placed at the periphery of the grain surfaces, the drastic microstructural change would be recognized. Although our research group has examined some addition of another element in CaFe$_2$O$_4$ preparation procedure, drastic changes in microstructure could not be obtained. However, recently, zirconium (Zr) addition was found to be a candidate for morphological control of CaFe$_2$O$_4$. Thus, the effect of Zr addition on the microstructure, morphology, and SSA of CaFe$_2$O$_4$ was intensively investigated and the characteristics of the products were examined in the present study.

Among the preliminary tested organic acids (citric, malic, tartaric, and malonic acids) as the precursor forming agents, malic acid was found to be the best agent to produce the high purity CaFe$_2$O$_4$ powder. Thus, malic acid was used in this study. Ca(NO$_3$)$_2$·4H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and malic acid in a 1:2:3 molar ratio were dissolved in ethanol to form the mixed solution. The addition of Zr was carried out by introducing Zr(OC(CH$_3$)$_3$)$_4$ solution into the above mentioned mixed solution. In the preliminary examination, the amount of Zr was settled at 5 and 10 mol % with respect to Fe. The mixed solution was dehydrated and heated on a hot plate to prepare the precursor. The precursor was calcined in the temperature range of 700 to 900°C in air for 12 h. The heating rate was 10°C/min in all cases. Powder X-ray diffraction (XRD) was carried out to analyze the crystal structure of the calcined powder. XRD patterns were recorded with Cu-Kα radiation under the following conditions: sweep rate of 2°/min,
30 kV, and 20 mA. PDF files were used to identify the crystal phases. The valence state were analyzed by X-ray photoelectron spectroscopy (XPS) under 10⁻⁶ Pa. XPS spectra were recorded by a Kratos AXIS-165 spectrometer with Al Kα radiation without pretreatment. The chemical composition was analyzed by X-ray fluorescence (XRF) under 10 Pa without pretreatment. XRF measurement was carried out by using Al, Mo, Cu as a secondary target. The SSA and textural properties (pore size, pore volume, and distribution) of materials were evaluated by the gas adsorption-desorption isotherms of N₂ at −196°C following the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The microstructure of the sample was observed by a field-emission scanning electron microscope (FE-SEM).

XRD peaks of Zr-unadded CaFe₂O₄ powder calcined at 700°C could be ascribed to CaFe₂O₄ phase [Fig. 1(a)]. The lattice parameters were calculated to be a = 0.92281, b = 1.07050, and c = 0.30185 nm, which were in good agreement with the reference value (PDF No. 00-032-0168). On the other hand, the XRD peaks of Zr-added products could also be ascribed to CaFe₂O₄ phase, and small impurity peaks appeared in the Zr-added CaFe₂O₄ powders in the 2θ range of 20 to 50° as indicated in Figs. 1(b) and 1(c). These diffraction peaks of impurities phases were identified as the Ca₂Fe₂O₅ and CaZrO₃ phases. When the 5 and 10 mol % Zr-added CaFe₂O₄ precursors were calcined at 900°C, it was found that those small peaks mainly arose from the CaZrO₃ phase. The mean crystallite size of the CaFe₂O₄ phase was estimated from the full width at half maximum of the (112) diffraction peak at 2θ = 33.5° by using the Scherrer’s equation. For the 700°C-calcined products, the mean crystallite sizes were estimated to be 49.7, 32.0, and 27.7 nm for unadded, 5, and 10 mol % Zr-added CaFe₂O₄, respectively. Also, the mean crystallite sizes of the 900°C-calcined products were estimated to be 60.5, 37.8, and 37.7 nm, respectively. Apparently, the crystallite growth of CaFe₂O₄ was suppressed by Zr-addition. Figure 2 shows the relationship between lattice parameters of CaFe₂O₄ and the amount of Zr additives (○: 700°C, □: 900°C).

CaFe₂O₄ crystal consists of eight-fold-coordinated Ca atoms and distorted FeO₆ octahedra. The ionic radii of Ca²⁺, Fe³⁺, and Zr⁴⁺ were reported as 1.12, 0.645, and 0.84 Å, respectively.
Therefore, when Fe\(^{3+}\) was replaced by Zr\(^{4+}\), the lattice parameters would increase with increasing the amount of Zr addition from only a viewpoint of ionic radii. However, in this case, Fe\(^{3+}\) in the CaFe\(_2\)O\(_4\) with the coordination number of 6 is replaced by Zr\(^{4+}\) of the coordination number 8. Thus the changes of lattice parameters were quite complicated. The lattice parameters of 700°C-calcined CaFe\(_2\)O\(_4\) were almost unchanged until 5 mol% Zr-addition and only parameter \(b\) decreased gradually. It is noted that the significant impurities were recognized for the 700°C-calcined CaFe\(_2\)O\(_4\). Thus it is speculated that the small amount of the added Zr was doped in CaFe\(_2\)O\(_4\) and the large amount of Zr was segregated at the periphery or surface of CaFe\(_2\)O\(_4\) grains. Also it should be noted that, although all impurities were not identified, at least, CaZrO\(_3\) was recognized at 900°C-calcined CaFe\(_2\)O\(_4\). Thus, the amount of Zr-doping seems to be regulated. The irregular change of parameters at 900°C-calcined samples were remained to be investigated, however, solubility limit of Zr into CaFe\(_2\)O\(_4\) was found to be small.

Figure 3 shows XPS spectra of Ca 2p, Fe 2p, O 1s, and Zr 3p for 5 mol% Zr-added CaFe\(_2\)O\(_4\) powder calcined at 700°C were compared with those for Zr-unadded product (pure CaFe\(_2\)O\(_4\) powder). The binding energy was corrected with respect to the C 1s signal centered at 285.0 eV. For the O 1s signal, there were two components at approximately 529.5 and 531.1 eV. The former corresponds to the lattice oxygen and the latter corresponds to carbonate formed at the surface of CaFe\(_2\)O\(_4\).\(^{16}\) The binding energies of the Ca 2p, Fe 2p, and Zr 3p spectra are in good agreement with those of the Ca\(^{2+}\), Fe\(^{3+}\), and Zr\(^{4+}\) valence states,\(^{17-19}\) Satellite Fe 2p peaks were also observed in the range of 716.0 to 721.0 eV, indicating that Fe\(^{3+}\) is dominant in the pure and Zr-added samples. When Zr\(^{4+}\) was incorporated into CaFe\(_2\)O\(_4\) phase, the reduction of Fe\(^{3+}\) to Fe\(^{2+}\) would be taken place for charge compensation, however, the small spectrum originated from Fe\(^{2+}\) could not be separated from dominant Fe\(^{3+}\) spectrum. The XRF measurement revealed that the content of Zr species in the 5 and 10 mol% Zr-added CaFe\(_2\)O\(_4\) were 5.5 and 9.3 mol%, respectively.

The nitrogen adsorption-desorption isotherms for unadded and Zr-added powders were classified as type IV by the Brunauer-Emmett-Teller (BET) scheme (Fig. 4).\(^{20}\) This result means that the examined three kinds of powders have mesoporous structures. The isotherm of 5 mol% Zr-added CaFe\(_2\)O\(_4\) indicated a characteristic nitrogen condensation-evaporation step and the volume adsorbed was 6.6 cm\(^3\) (STP) g\(^{-1}\) at a relative pressure of 0.84. The isotherm of 10 mol% Zr-added CaFe\(_2\)O\(_4\) exhibited the adsorbed volume of 13.1 cm\(^3\) (STP) g\(^{-1}\) at 0.79. Meanwhile, the isotherm of unadded CaFe\(_2\)O\(_4\) showed the similar step and the volume adsorbed was 9.2 cm\(^3\) (STP) g\(^{-1}\) at relatively higher pressure of 0.94. Furthermore, the hysteresis loops associated with capillary condensation were observed for all sample powders, as shown in Fig. 4. According to the de Boer's classification,\(^{21}\) it was found that unadded and 10 mol% Zr-added CaFe\(_2\)O\(_4\) powders contained wedge-shaped pores with open ends (type C), whereas 5 mol% Zr-added CaFe\(_2\)O\(_4\) had cylindrical pores (type A). Only the 5 mol% Zr-added product was classified in cylindrical pores containing type. We consider, at this moment, the solubility limit of Zr-doping into CaFe\(_2\)O\(_4\) phase is around 5 mol%, however, further detailed investigation is required.

The BJH pore size distribution was calculated from a branch of the nitrogen desorption isotherms (Fig. 5). For Zr-unadded
in the mother material of CaFe$_2$O$_4$ was speculated to work as the morphology of each grain is irregular shape. When 5 mol CaFe$_2$O$_4$, and (c) 10 mol CaFe$_2$O$_4$. The SSA of a maximum in 5 mol approximately 5 mol

heating at 700°C in air for 12 h.

CaFe$_2$O$_4$, a large peak was observed in the range of 10 to 40 nm and the representative pore size was 25 nm. The mean pore size of 5 mol % Zr-added CaFe$_2$O$_4$ was around 22 nm. The pore volume decreased when Zr was added to CaFe$_2$O$_4$. The SSA of unadded CaFe$_2$O$_4$ powder calcined at 700°C was calculated to be 8.0 m$^2$ g$^{-1}$, by applying the least squares method to the BET plot. When 5 mol % Zr was added to CaFe$_2$O$_4$, the BET surface area increased drastically in 18.9 m$^2$ g$^{-1}$, whereas it decreased at 10 mol % Zr-addition in 8.9 m$^2$ g$^{-1}$.

SEM was used to investigate why the BET surface area reaches a maximum in 5 mol % Zr-added CaFe$_2$O$_4$ (Fig. 6). Zr-unadded CaFe$_2$O$_4$ powder consists of tightly interconnected grains and the primary particle size is in the range of 0.2–0.4 μm. Moreover, the morphology of each grain is irregular shape. When 5 mol % Zr was added to CaFe$_2$O$_4$, three-dimensional network connecting of small grains was formed to have porous microstructure. On the other hand, 10 mol % Zr-added CaFe$_2$O$_4$, the three-dimensional network structure could not be recognized and tightly interconnected grains appeared again. The change in the microstructure is consistent with the 5 mol % Zr-added CaFe$_2$O$_4$ powder having the largest specific surface area among the three kinds of samples examined. The solubility limit of Zr into CaFe$_2$O$_4$ is estimated approximately 5 mol % as mentioned above. Thus, the added Zr in the mother material of CaFe$_2$O$_4$ was speculated to work as the network structure assisting material. However, the excess amount of Zr-addition could not be doped in the mother material due to the solubility limit. The excess Zr might lead to the formation of Zr-containing impurities at the grain boundaries resulting in tightly interconnected grains. The relationships among morphology, sintering behavior, and textural characters should be further investigated, however, some relations could be described in this report.

In conclusion, unadded and Zr-added CaFe$_2$O$_4$ could be prepared at 700°C which is almost 200°C lower than that of conventional solid-state reaction method. The morphology of 5 mol % Zr-added product revealed characteristic porous structure of smaller grains connected three-dimensional network structure resulting in higher specific surface area compared with unadded and 10 mol % Zr-added products. From the XPS measurements, there were no notable changes in valence state for all constituent elements. Further investigation is required to clarify the drastic morphological change, however, the present study might produce one of the strategies to enhance adoptability of CaFe$_2$O$_4$ materials for surface-related function driven devices. The investigation on adoptability and performance of 5 mol % Zr-added product for various practical applications is further work to activate the material’s characteristics.

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